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Investigating membrane selectivity based on polymer swelling

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ABSTRACT

Nanofiltration has many potential applications as a separation technology for processes that use mixtures of aqueous and organic solvents, for example alcohol/water mixtures. Membrane systems are well established for separations carried out in aqueous media, however they have seen a much slower rate of uptake in non-aqueous processes or with aqueous/organic mixtures. This is because the interaction between membrane and solvent(s) dictates both the permeability and selectivity, and there is currently limited criterion for identifying the theoretical performance of a membrane based on the properties of a bulk polymeric material. The small numbers of commercial successes to date have arisen from empirical findings, with no agreed methodology by which new candidate membrane materials can be identified.

New membrane materials are required to exhibit a high permeability along with the selectivity demanded by the application. Permeability can be relatively easily manipulated using engineering solutions such as large surface areas, or very thin active separation layers. Selectivity, however cannot be manipulated in such an intuitive fashion, with the mixture type and composition, pressure and polymer characteristics all reported to be major factors. This work investigates the factors which influence the inherent selectivity of polymeric materials, and the link to nanofiltration processes. The aims of this study are to investigate the effectiveness of current theoretical and predictive tools, and to establish a technique to evaluate polymeric materials without having to fabricate a membrane.

Two polymers were chosen for study which are at opposing ends of the permeability/selectivity spectrum. Polydimethylsiloxane (PDMS) and poly (vinyl alcohol) (PVA) membranes have been previously investigated in several separations involving organic-water mixtures. The materials were characterized using GPC and ATR-FTIR

techniques, with ATR-FTIR further used to quantify the crosslinking content of the polymers. The total swelling degree and the inherent separation that occurs upon swelling with solvent mixtures was studied for a range of model and industrially-relevant systems, using polymer materials fabricated under different conditions.

It was found that the selectivity of the polymer was a highly non-linear function of mixture type and concentration. PDMS and PVA were shown to change their affinity toward mixture components depending on the concentration, and it was hypothesized that this is due to competing mechanisms based on both molecular size and polarity. Selectivity was shown to be less dependent on the applied pressure and the degree of crosslinking, with the polymer type and mixture composition the two most dominant factors.

The Flory-Huggins model was evaluated and found to give an extremely poor prediction of the selectivity in all the polymer-solvent systems studied. Further analysis was carried out using chemical potential and activity coefficient models in order to establish the sorption coefficient for future comparison with membrane filtration data. One of the key outcomes of this work is the measurement of sorption coefficients at varying composition and pressure, which can subsequently be used with existing Solution-Diffusion and Pore-Flow filtration models with greater confidence than has been possible to date.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	I
ABSTRACT	II
Chapter 1 INTRODUCTION	1
1.1 Background and industrial context.....	1
1.2 Study aims and objectives.....	1
1.3 Thesis overview	2
Chapter 2 LITERATURE REVIEW	4
2.1. Current industrial processes producing organic/water streams	4
2.1.1 Fermentation	4
2.1.2 Hydrocarbon processing	5
2.1.3 Pharmaceutical industry.....	5
2.1.4 Food processing.....	6
2.1.5 Nuclear fuel manufacturing	7
2.2 Existing separation technologies for aqueous organic systems.....	7
2.2.1 Distillation	8
2.2.2 Liquid-liquid extraction	8
2.2.3 Adsorption.....	9
2.2.4 Membrane separation	10
2.3 Membrane separation processes.....	11
2.3.1 The history of membrane development	11
2.3.2 Classification of membrane processes	12
2.3.3 Classification of membranes.....	14
2.3.4 Membrane materials	19
2.3.5 Transport processes and mechanisms	24

2.3.6 Separation mechanisms.....	30
2.4 Methods to quantify membrane selectivity.....	33
2.4.1 Factors affecting membrane selectivity	33
2.4.2 Membrane performance data.....	34
2.4.3 Organic/organic systems	36
2.5 Key criteria for membrane selection.....	38
2.5.1 Hydrophilicity/hydrophobicity and surface characterisation.....	38
2.5.2 Membrane swelling.....	39
2.5.3 Solubility parameters	41
2.6 Polymer swelling.....	44
2.6.1 Swelling mechanisms.....	44
2.6.2 Swelling equilibrium and membrane selectivity	47
2.6.3 Quantification of membrane selectivity.....	48
2.6.4 Sorption coefficient.....	48
2.6.5 Flory-Huggins theory	51
Chapter 3 EXPERIMENTAL	57
3.1 Introduction.....	57
3.2 Preparation of PDMS	57
3.2.1 Materials	57
3.2.2 Crosslinking reaction	58
3.2.3 Different crosslinking contents.....	60
3.2.4 Washing.....	61
3.2.5 Validity of swelling measurement technique.....	64
3.3 Preparation of crosslinked polyvinyl alcohol PVA	66
3.3.1 Materials	66

3.3.2 PVA crosslinking reaction.....	67
3.3.3 PVA different crosslinking content.....	71
3.3.4 PVA washing.....	72
3.3.5 Validity of swelling measurement technique.....	74
3.4 Swelling in pure solvents.....	76
3.4.1 Materials	76
3.4.2 Polymer swelling measurements in pure solvents.....	76
3.5 Swelling in solvent mixtures	76
3.5.1 Method	76
3.5.2 Concentration measurement	77
3.6 Effect of pressure on polymer swelling	79
3.6.1 Experimental apparatus.....	79
3.6.2 Experimental procedure.....	80
3.6.3 Measurement method.....	81
Chapter 4 POLYMER CHARACTERISATION.....	83
4.1 Introduction.....	83
4.2 Equipment and method	83
4.2.1 Gel-permeation chromatography (GPC).....	83
4.2.2 Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).	86
4.3 Results and discussion	88
4.3.1 GPC for RTV615A and RTV615B.....	88
4.3.2 ATR-FTIR characterization	90
4.4 Conclusions.....	96
Chapter 5 SWELLING OF POLYMERS IN PURE SOLVENTS	98

5.1 Introduction.....	98
5.2 Polymer swelling in pure solvents	98
5.2.1 PDMS in pure solvents	98
5.2.2 PVA in pure solvents	101
5.3 Prediction of polymer swelling in different solvents	102
5.3.1 Solubility parameter	102
5.3.2 Different components of solubility parameter.....	106
5.3.3 Polymer/solvent interaction parameter, χ	110
5.4 Conclusions.....	113
Chapter 6 EFFECT OF SOLVENT MIXTURES ON POLYMER SELECTIVITY	114
6.1 Introduction.....	114
6.2 PDMS in ethanol/n-alkanes mixtures	114
6.2.1 Total swelling degree	114
6.2.2 Change in composition due to swelling	115
6.2.3 Sorption coefficient (K_i) of PDMS in ethanol/n-alkanes.....	119
6.2.4 Application of Flory-Huggins theory to the ternary system	121
6.3 Sensitivity analysis.....	124
6.4 PDMS in alcohol/water.....	126
6.4.1 Total swelling degree	126
6.4.2 Change in composition due to swelling.....	127
6.4.3 Sorption coefficient (K) in alcohol/water mixtures.....	131
6.4.4 Application of Flory-Huggins theory to ternary system	133
6.5 PVA in alcohol/water.....	136
6.5.1 Total swelling degree	136
6.5.2 Change in composition due to swelling.....	137

6.5.3 Sorption coefficient (K) of PVA in alcohol/water	140
6.5.4 Application of Flory-Huggins theory to ternary system	141
6.6 Comparison between sorption coefficient in PDMS and PVA.....	143
6.6.1 Ethanol/water system	143
6.6.2 Isopropanol/water system	144
6.7 Conclusions.....	146
Chapter 7 EFFECT OF POLYMER CROSSLINKING CONTENT ON SELECTIVITY	148
7.1 Introduction.....	148
7.2 Comparison with literature	148
7.3. Alcohol/water sorption in PDMS	149
7.3.1 Effect of crosslinking content on swelling degree	149
7.3.2 Effect of crosslinking content on alcohol sorption.....	151
7.3.3 Alcohol sorption coefficient.....	154
7.4. Alcohol/water sorption in PVA.....	155
7.4.1 Effect of crosslinking content on total swelling degree.....	155
7.4.2 Effect of crosslinking content on alcohol sorption.....	157
7.4.3 Alcohol sorption coefficient.....	160
7.5. Sorption coefficients of alcohols in PDMS and PVA	163
7.6 Conclusions.....	165
Chapter 8 EFFECT OF PRESSURE ON POLYMER SELECTIVITY.....	166
8.1 Introduction.....	166
8.2 Effect of pressure on PDMS swelling in different solvents.....	166
8.3 Effect of pressure on PDMS swelling in alcohols.....	169
8.3.1 Effect of pressure on PDMS swelling in alcohol/water mixtures	171

8.3.2 Effect of applied pressure on alcohol concentration	172
8.3.3 Effect of pressure on alcohol sorption coefficient.....	175
8.4 Effect of pressure on PVA swelling in alcohols	176
8.4.1 Effect of pressure on PVA swelling in alcohol/water mixtures.....	176
8.4.2 Effect of applied pressure on alcohol concentration	177
8.4.3. Alcohol sorption coefficient (K) for PVA in alcohol/water mixture	180
8.5. Sorption coefficients in PDMS and PVA.....	181
8.6 Explaining the effect of pressure on alcohol sorption coefficient.....	182
8.6.1. Numerical analysis to identify the effect of fugacity	183
8.6.2 The activity coefficient	185
8.7 Conclusions.....	189
Chapter 9 CONCLUSIONS AND FUTURE WORK.....	190
9.1 Conclusions.....	190
9.2 Future work.....	193
REFERENCES	195
APPINDIX 1.....	227

LIST OF FIGURES

Figure 2-1 Dead-end and cross-flow filtration processes	13
Figure 2-2 Effect of concentration polarisation on concentration profile for filtration	14
Figure 2-3 Membrane classifications and their application range	15
Figure 2-4 Schematic of the principal types of membranes structure.....	20
Figure 2-5 Transport through a membrane	24
Figure 2-6 The transportation mechanism of mixtures based on the pore flow model	27
Figure 2-7 Transport of a component through a membrane according to the pore flow model.....	28
Figure 2-8 Transport of a component through a membrane according to the solution diffusion model.....	29
Figure 2-9 Alcohol permeability and selectivity	35
Figure 2-10 Polymer and solvent swelling mechanism (absorption, penetration and expansion).....	46
Figure 2-11 Swelling mechanism of membrane pore and rejection mechanism.....	46
Figure 3-1 Structure of RTV615A showing the PDMS reactive vinyl end groups.....	57
Figure 3-2 Structure of RTV615B showing the PDMS SiH ₃ end functional groups.....	58
Figure 3-3 Schematic illustrating crosslinking reaction of PDMS	59
Figure 3-4 Sample swelling data for PDMS washed for 3 cycles in toluene	62
Figure 3-5 Drying of swollen PDMS over time	65
Figure 3-6 Crosslinking reaction between PVAc and GA and the formation of structure 1 (acetal ring groups).....	68
Figure 3-7 Crosslinking reaction between PVAc and GA and the formation of structure 2 (ether linkages)	69

Figure 3-8 Crosslinking reaction between PVAc and GA and the formation of structure 3 (aldehyde linkage formation).....	70
Figure 3-9 Swelling of crosslinked PVA in 3 cycles over three time intervals	73
Figure 3-10 Drying of crosslinked PVA from water over time	75
Figure 3-11 Refractive index plotted against alcohol concentration for ethanol/water and isopropanol/water mixtures.....	78
Figure 3-12 Refractive index plotted against ethanol concentration for ethanol/hexane and ethanol/heptane mixtures	79
Figure 3-13 Schematic of the pressure cell and reservoir cell.....	80
Figure 4-1 Schematic of a GPC column during operation.....	84
Figure 4-2 Schematic of ATR-FTIR during operation	87
Figure 4-3 GPC for RTV615A (pre-polymer)	89
Figure 4-4 GPC for RTV615B (crosslinking agent)	89
Figure 4-5 FTIR spectra of RTV615A.....	91
Figure 4-6 FTIR spectra of RTV615B	91
Figure 4-7 ATR-FTIR spectra of different crosslinked PDMS.....	92
Figure 4-8 FTIR spectra for different crosslinked PVA.....	95
Figure 5-1 Swelling degree of PDMS in different solvents over time (Group 1).	99
Figure 5-2 Swelling degrees of PDMS in different solvents over time (Group 2).	99
Figure 5-3 Swelling degree of PVA over time.....	101
Figure 5-4 Relationship between swelling degree of PDMS and PVA in various solvents with the deviation between solvent and polymers solubility parameters	104
Figure 5-5 Relation between PDMS swelling degree, and δ_r , and δ_h for different solvents	107

Figure 5-6 Relation between PVA swelling degree, and δ_r , and δ_h for different solvents	108
Figure 5-7 Solubility parameters of pure solvents versus polymer solvent interaction parameters of PDMS. The dashed line indicates the solubility parameter of PDMS ($\delta = 14.9 \text{ MPa}^{0.5}$)	111
Figure 5-8 Solubility parameters of pure solvents versus PVA/solvent interaction parameters. The line indicates the solubility parameter of PVA ($\delta = 39.07 \text{ MPa}^{0.5}$)	112
Figure 6-1 PDMS swelling degree over different ethanol concentrations in ethanol/n-alkanes mixtures	115
Figure 6-2 Equilibrium ethanol, n-heptane and PDMS concentration in swollen polymer at different ethanol concentrations.	117
Figure 6-3 Ethanol, n-hexane and PDMS concentration at equilibrium in swollen polymer at different ethanol concentrations.	117
Figure 6-4 Ethanol concentration in liquid within swollen PDMS. The straight line ($y = x$) represents a selectivity of zero.	118
Figure 6-5 Ethanol sorption coefficient for ethanol/n-alkanes mixtures.	119
Figure 6-6 Ethanol activity in liquid and ethanol activity calculated using the Flory-Huggins model, at different ethanol concentration.	123
Figure 6-7 Ethanol activity in liquid and ethanol activity calculated using the Flory-Huggins model, at different ethanol concentration.	123
Figure 6-9 Swelling degree plotted against alcohol concentration in alcohol/water mixtures	126
Figure 6-10 Relationship at equilibrium between isopropanol, water, and PDMS concentrations in the swollen polymer.	128

Figure 6-11 Relationship between ethanol, water, and PDMS concentrations at equilibrium in the swollen polymer.	128
Figure 6-12 Alcohol concentration in the polymer plotted against the equilibrium concentration in the liquid phase. The straight line ($y=x$) represents a selectivity of zero	130
Figure 6-13 Alcohol sorption coefficient at different alcohol/water mixtures....	132
Figure 6-14 Isopropanol activity in liquid and isopropanol activity calculated using Flory-Huggins model.....	134
Figure 6-15 Ethanol activity in liquid and ethanol activity calculated using Flory-Huggins model.....	135
Figure 6-16 Total swelling degree at different alcohol concentrations in alcohol/water mixtures.....	136
Figure 6-17 Relationship at equilibrium between ethanol, water, and PVA concentration in swollen polymer	138
Figure 6-18 Relationship between equilibrium isopropanol, water and PVA concentrations in swollen polymer	138
Figure 6-19 Alcohol concentrations in the liquid inside swollen PVA versus alcohol concentration in the liquid phase. The straight line ($y=x$) represents a selectivity of zero	139
Figure 6-20 Relationship between alcohol sorption coefficient and alcohol concentration	140
Figure 6-21 Relationship between Flory-Huggins model and experimental ethanol activity	141
Figure 6-22 Relationship between Flory-Huggins model and isopropanol activity	142

Figure 6-23 Comparison between PDMS and PVA ethanol sorption coefficient in ethanol/water mixtures.....	143
Figure 6-24 Comparison between PDMS and PVA isopropanol sorption coefficient in isopropanol/water mixtures.....	145
Figure 7-1 Relationship between swelling degree of PDMS in hexane at different crosslinking content, and comparison with literature.	149
Figure 7-2 Swelling degree in ethanol and isopropanol	150
Figure 7-3 Swelling degree in alcohol/water mixtures	150
Figure 7-4 Effect of crosslinking content on alcohol sorption in swollen PDMS.....	153
Figure 7-5 Relation between crosslinking content and alcohol sorption coefficient for ethanol/water and isopropanol/water mixtures.....	154
Figure 7-6 Swelling in water and alcohol/water mixtures at different crosslinking contents.	156
Figure 7-7 Effect of PVA crosslinking content on concentration within liquid in swollen PVA	158
Figure 7-8 Relation between crosslinking content and alcohol sorption coefficient in ethanol/water and isopropanol/water mixtures.....	160
Figure 7-9 Comparison of PDMS and PVA polymers in 30% aqueous alcohol mixture for different polymer crosslinking contents.....	163
Figure 8-1 Comparison of swelling data with	167
Figure 8-2 Effect of applied pressure on swelling degree of PDMS in ethanol and isopropanol.....	170
Figure 8-3 Effect of pressure on the swelling degree of PDMS in 30% alcohol/water mixtures.....	171

Figure 8-4 Effect of applied pressure on alcohol concentration within liquid in swollen PDMS.....	174
Figure 8-5 Relationship between applied pressure and alcohol sorption coefficient for 30% alcohol in aqueous mixtures	175
Figure 8-6 PVA swelling degree in ethanol and isopropanol at different pressure	176
Figure 8-7 Effect of applied pressure on the swelling degree of PVA in 30% alcohol/water mixtures.....	177
Figure 8-8 Effect of applied pressure on alcohol concentration within liquid in swollen PVA from alcohol/water mixtures.....	179
Figure 8-9 Relationship between applied pressure and the alcohol sorption coefficient from aqueous alcohol mixture	180
Figure 8-10 Comparison between PDMS and PVA polymers in aqueous alcohol mixture under different pressures.....	181
Figure 8-11 Relationship between applied pressure and alcohol fugacity for ethanol and isopropanol.....	184
Figure 8-12 Activity coefficient profile through the swollen polymer due to increasing pressure	186
Figure 8-13 Simulation of pressure driven permeation of one component through a membrane based on solution diffusion model.....	187
Figure 8-14 Simulation of pressure driven permeation of a one-component through a membrane based on pore flow model	188

Chapter 1 INTRODUCTION

1.1 Background and industrial context

One of the major challenges of the 21st century, especially in developing countries, is the production and supply of potable water. The major reasons for the aggravated water situation in developing countries are inadequate supply coupled with increasing water demand due to rapid population growth and industrialisation. Hence, there is strong emphasis on production of desalinated water and reclamation of wastewater for reuse [1-3].

In order to remain competitive, industry has to constantly review its production methods for the reclamation of wastewater for reuse. Industry continuously invests in research where new technology is introduced to improve production performance and reduce costs. The synthesis of chemical products requires chemical, physical, and/or biological separation, which can consume large amounts of energy and require the use of organic solvents. The need to minimise hydrocarbon losses, which are a source of energy, is especially critical.

A recent report on the generation of liquid industrial waste in the USA revealed that there are 7,000 plants in the USA, each discharging more than one million gallons of wastewater per day [4]. UK industries produce around 400,000 tonnes per year of industrial wastewater with an estimated disposal cost of £8 - 16 million in 2000 [5]. A similar amount of industrial waste is produced in France, Germany and Italy.

The increase in waste disposal costs contributes to the pressure on industry from regulators to take more responsibility for their waste. Therefore, engineering industries face a particular challenge to treat the waste effluent that they produce.

Improved separation technologies can be expected to reduce the amount of waste emissions, particularly in the area of separation from dilute streams. Industrial wastes may contain oil, organics and grease as common pollutants from a wide range of industries. The composition of wastewater generated varies greatly by industry, which can no longer sustain disposal of valuable hydrocarbons in waste streams [1, 6].

Manufacturing processes were reviewed to identify hydrocarbon-containing wastewater streams. Several processes were identified within fermentation, and in the petrochemicals, petroleum refining, pharmaceutical, food industries, as well as nuclear fuel manufacturing. Various separation technologies are utilised to separate and purify products, recover and recycle valuable components, and separate contaminants from dilute streams prior to discharge. These processes are energy intensive, and there are major opportunities for new technologies that conserve energy, recover valuable process chemicals, and reduce waste and emissions. Distillation is the most widely used separation process, and accounts for as much as 49% of the industry's overall energy use, and 90 to 95% of separation energy. Moreover, distillation columns often operate with considerably low thermodynamic efficiency [7]. Other separation technologies used, include solvent extraction, absorption, adsorption, crystallisation, drying, and more recently membrane processes. This project aims to investigate the use of membranes in industrial streams that contain organic mixtures, focusing on organic and water mixtures.

1.2 Study aims and objectives

This work investigates the applicability of nanofiltration (NF) to the separation of aqueous organic solutions. In this study, no actual separation is performed with such a system, but the work aims to develop laboratory-based techniques that will estimate the selectivity of the polymer used based on swelling, rather than having to fabricate a membrane and test it.

No method to quantify or estimate the selectivity of a polymer without making a membrane and carrying out a filtration test has been previously reported in the literature.

Transport mechanisms through membranes are complicated, because of the coupling that exists between the sorption and diffusion process. This work attempts to separate them, and to study the influence of sorption alone on membrane selectivity. It is anticipated that suitable candidate membrane materials can be identified by assessing the inherent selectivity of the polymers during this work. The objectives of the study are:

1. Identify polymeric materials that are suitable for use as nanofiltration membranes, and characterize their physical and chemical properties and degree of crosslinking..
2. Establish and validate experimental techniques to quantify the separation of solvent mixtures that occurs due to swelling at atmospheric and elevated pressures.
3. Investigates the factors which influence the inherent selectivity of polymeric materials such as mixture type and composition, pressure and polymer characteristics.
4. Explores the effectiveness of current theoretical and predictive tools.

1.3 Thesis overview

This thesis presents a systematic study to investigate the selectivity of organic-water and alkane-alcohol mixtures based on polymer swelling. Chapter 1 presents the background and justification for the project, industrial context and the aims and objectives. A critical literature review is included in Chapter 2, which covers alternative separation techniques and the potential advantages offered by membrane processes. The role of polymer swelling in determining the selectivity is discussed, along with current methods and models to quantify the interaction between solvents and polymers. Chapter 3 describes the materials, equipment and protocols adopted for each experiment in this study. In this chapter the

description of a novel apparatus used for swelling measurement under different pressures is presented.

The results from this study are presented in Chapters 4-8. Chapter 4 covers the characterization of the materials manufactured in this study. The swelling of the polymers in pure solvents is included in Chapter 5, which provides the key validations of the experimental techniques used in this work. The novel aspects of this thesis appear in Chapters 6-8, where the selectivity that occurs due to swelling is presented based on changes in composition (Chapter 6), crosslinking (Chapter 7) and pressure (Chapter 8). Chapter 8 also introduces the relationship between applied pressure and the sorption coefficient which could be used to further develop existing modelling approaches. Chapter 9 summarises the findings and conclusions of this research, the industrial implications and avenues for further work.

Chapter 2 LITERATURE REVIEW

2.1. Current industrial processes producing organic/water streams

2.1.1 Fermentation

Biomass has potential as an alternative energy source to supplement or replace fossil fuels. A fermentation process is required to convert the biomass into a useful energy source. For example, ethanol in Brazil is produced from sugar cane fermentation, mainly for use as an additive to gasoline for motor vehicles. The fermentation process has been extensively researched for ethanol production, which is the main product and it is increasingly important due to its possible application in liquid fuels [8]. For example, ethanol is increasingly used in gasoline formulation for octane enhancement. According to fuel specifications, the water content of ethanol to be blended with gasoline should be less than 1.3 wt% [9]. Ethanol and water form azeotropes at 4.4 wt% of water at atmospheric pressure, which makes it difficult to enrich ethanol to high concentrations by a simple distillation process. An azeotropic mixture exists when the composition of the vapour phase is identical to the liquid phase, and such a mixture cannot be further enriched using standard distillation techniques. Membranes can be used to separate azeotropes as the separation in membrane process is based on selective solution and diffusion, not the relative volatility as in distillation.

The biomass fermentation process produces around 3–8 wt% ethanol, and should be followed by a purification step to raise ethanol concentration to >98.7 wt%, suitable for use as an energy source [10]. Separation of ethanol from water poses a significant problem for industry due to its high price as a fuel, and competition from other products in its gasoline applications [11].

The economics of production of this renewable fuel have been a challenge for many manufacturing facilities. Researchers have suggested that improvements to the fuel ethanol production process resulting in savings as low as 0.02–0.05 US\$ per gallon could significantly increase demand [12]. The improvement of ethanol production is by conversion of the batch or sequential-batch fermentation process to a continuous fermentation process. This can be achieved by the addition of an ethanol extraction operation within the fermentation step.

2.1.2 Hydrocarbon processing

The hydrocarbon processing industry produces large quantities of oily wastewater. Hydrocarbon production processes include petroleum refining, petrochemical processing and related chemical processing. Therefore, wastewater may contain different types of hydrocarbons ranging from ethanol, propanol, alkanes and many other organic compounds. Ethylene and propylene, in particular, are the most important chemical feedstocks used in the petrochemical industry. They are used for the production of polyethylene, polypropylene, styrene, acrylonitrile, and isopropanol [13]. Large quantities of these chemicals are used with aqueous systems, and consequently large amounts of wastewater are generated. Hence, petrochemical waste streams may contain isopropanol, ethylene and propylene compounds [14]. Low-cost hydrocarbon separation technologies are required to recover these organics from wastewater to increase industry compliance and reduce the economic and environmental impact.

2.1.3 Pharmaceutical industry

The manufacturing of pharmaceutical products is often performed using different organic solvent such as ethanol, isopropanol, and dichloromethane [15]. Isopropanol is also used

as a solvent in the analysis and purification of polypeptides by the chemical and analytical industry [16], which yield large amounts of isopropanol and water waste.

The recycle and reuse of solvents is especial challenging as most pharmaceutical applications require high purity, i.e. 99.5% isopropanol. However, isopropanol forms an azeotrope with water at 88 wt%, which makes separation from water difficult using conventional distillation processes [17-18]. The need to reduce hydrocarbon losses and recover ethanol and isopropanol from wastewater is desirable from an economic and environmental standpoint, but technically difficult to achieve using current technologies.

2.1.4 Food processing

In food processing plants the use of large volumes of water to manufacture products and clean plant equipment yields large amounts of wastewater. This adds to the financial and ecological burden of food processing, as well as adversely affecting the environment. The use of ethanol, isopropanol, and hexane for refining vegetable oil is common [19]. Large quantities of water and chemicals are used, resulting in large amounts of wastewater. Wastewater from food processing contains ethanol and other valuable hydrocarbons, which must be recovered before disposal. For example, wastewater from the dairy industry is 140 m³/m³ of milk, the brewing industry is 10-15 m³/m³ of beer, and the sugar industry is 8 m³/ ton of sugar [20]. Currently, an industrial process for pectin production from mandarin peels requires large amounts of ethanol for purification of pectin, and it results in a large amount of ethanol in wastewater [21]. The composition of the wastewater generated varies greatly by food processing industry, which can no longer allow disposal of ethanol, hexane and other hydrocarbons in their waste streams. In streams containing such effluent, treatment technologies should be employed to recycle valuable products, and produce potable water.

2.1.5 Nuclear fuel manufacturing

The nuclear fuel manufacturing process starts from the chemical conversion of uranium hexafluoride (UF_6) to obtain ammonium diuranate (ADU) which is converted to plates of uranium oxide [22]. The use of ethanol for washing of ammonium diuranate is common in nuclear fuel manufacturing. The washing process yields large amounts of ethanol and wastewater. Recycle and reuse of ethanol is especially critical to the economic viability of the process. The total amount of waste is 100 litres per kg of ADU produced [23]. The ethanol in the waste liquid effluent ranges from 15 to 30 wt%. In streams containing such effluent, the need to recover and recycle ethanol from such effluent is an economic and environmental necessity.

2.2 Existing separation technologies for aqueous organic systems

The most common separations technologies used in industry are distillation, liquid-liquid extraction, adsorption, and membrane processes. Separation operations can be classified into high-energy separation processes, such as distillation, and low-energy separation processes, such as membrane processes. In order to remain competitive, industrial separation technologies and production methods must be continuously reviewed, with high-energy separation processes replaced by low-energy process to improve production performance.

Distillation technologies are well established among industrial separation processes, and account for 49% of industrial separation energy consumption. Evaporation, crystallization, extraction, absorption, adsorption, solid-solid, solid-liquid, liquid-liquid extraction, and physical property-based operations accounts for 48% of industrial separation energy consumption. Membrane separation systems are low-energy separation processes,

accounting for less than 3% of energy consumption in industrial separations. Using low-energy separation processes could save >1 TBtu per year, which represents in excess of £30 million per year [1].

2.2.1 Distillation

Distillation is the separation of components from a mixture that depends on differences in their volatility. It is theoretically based on differences in the vapour-liquid equilibrium of components. It is the most widely used separation process for mixtures that can be vaporized, with approximately 40,000 distillation columns in operation in the United States alone [1]. Distillation processes are widely used for the separation of organic chemicals, and accounts for 90%–95% of all separations in the chemicals and petroleum refining industries. Distillation has many applications; for example, multi-component fractionation of crude oil, separation of air into nitrogen and oxygen, separation of ethyl benzene from styrene, and separation of alcohols from water. The advantages of distillation in wastewater treatment could be the production of pure water. This is one of the few practical ways to remove nitrates, chlorides, and other salts that standard filtration process could not completely remove. However, its disadvantages are the requirement for the heat of Vaporization to be overcome, low energy efficiency, thermal stability of compounds at their boiling points, and the need for heating and condensation equipment.

2.2.2 Liquid-liquid extraction

Liquid-liquid extraction is accomplished based on the difference in solubility of the mixture components in a solvent. The separation technique includes two immiscible liquid phases. One of the two phases, the solvent phase, extracts the solutes from the other liquid phase. There are two requirements for liquid-liquid extraction to be possible:

The components to be removed from the feed must preferentially distribute in the solvent. The feed and solvent phases must be essentially immiscible to achieve extraction. Liquid-liquid extraction is followed by solvent recovery. The raffinate (residual liquid) is cleaned up after the separation process. There is more than one possible method of purifying the solvent and raffinate, so liquid-liquid extraction design is specific to each application [24]. The advantages of liquid-liquid extraction are operation at low to moderate temperatures and near atmospheric pressure. However, the disadvantage is that a solvent recovery process is required after achieving separation, which can consume a significant amount of energy. A further disadvantage of liquid-liquid extraction is equipment size, as it uses a large solvent/sorbent reservoir. Liquid-liquid extraction is commonly used to separate azeotropes, where distillation cannot be used.

2.2.3 Adsorption

Adsorption is the accumulation of a component on the surface of a solid. Adsorption is based on the adsorbent's strong affinity for one or more components of the mixture to be separated. The adsorbate held by the solid surface can be subsequently desorbed, and the adsorbent regenerated for further adsorption. The collected component is followed by thermal or chemical recovery in a second operation, and the adsorbent is reused. The process is cyclic, alternating between adsorption and desorption. The desorption mechanism must overcome the attractive forces between the adsorbates and the adsorbent; this is achieved by raising the temperature, reducing the pressure, adding another component that competitively adsorbs with the adsorbate, or a combination of these strategies. Therefore adsorption/desorption design is specific to each application.

Adsorbent materials must have a high surface area per unit weight ($100 \text{ m}^2/\text{g}$ to $10,000 \text{ m}^2/\text{g}$) [25], which allows increased loading of adsorbate on its surface. The major

advantage of the adsorption processes is the ability to produce products with contaminant concentrations in the range of parts per billion and ability to operate at ambient temperature. However, the disadvantage of adsorption is the concentrations of components to be removed are limited to several hundred parts per million in fixed bed processes, so are of limited use when considering wastewater streams with more than 1 wt% of organic contaminants. Adsorption processes have been applied in many industries, such as gas and liquid purification, and are widely applicable throughout the chemical and petroleum industries.

2.2.4 Membrane separation

A membrane is defined as an engineered barrier, which separates two phases and restricts transport of various substances in a selective manner. The key property of a membrane is the ability to selectively control the permeation of a particular species through the system. The transportation (selectivity and permeability) of components between feed and retentate phases is controlled by the membrane material and the operating conditions [26]. Membrane processes do not generally include a phase change (with the exception of pervaporation systems), and do not therefore require the heat of vaporisation to be overcome as in distillation. This means that the membrane process can achieve a separation using much less energy than an equivalent distillation process. Membrane system performance is a function of the process operating conditions, the nature and chemical composition of the process stream and the chemical composition and morphology of the membrane material [27]. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure. It can be solid or liquid, and can carry a positive or negative charge or be neutral or polar. Transport through a membrane

can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient [24].

A significant amount of current research focuses on developing new membrane materials and morphology, though some research is also directed at controlling specific process conditions and process stream composition in order to take advantage of existing membrane materials [24].

2.3 Membrane separation processes

2.3.1 The history of membrane development

The historical development of membrane phenomena can be traced to the eighteenth century, when Abb'e Nolet [28] used the word 'osmosis' to describe permeation of water through a diaphragm in 1748. Membranes were used only in the laboratory for simple separation processes, and had no industrial or commercial uses through the nineteenth and early twentieth century. The development of membrane preparation was in 1907, when Bechhold [29] prepared nitrocellulose membranes of graded pore size. In the early 1930s, other researchers, particularly Elford [30], Zsigmondy and Bachmann [31] and Ferry [32], improved Bechhold's technique, and introduced commercial porous membranes. The generic discovery transformed membrane separation from a laboratory to an industrial process in 1960, when Loeb–Sourirajan [33] made the first reverse osmosis membranes. The Loeb–Sourirajan reverse osmosis membrane flux was 10 times higher than that of any previous membrane, and this development made reverse osmosis a potentially practical method for desalinating water on an industrial scale. A significant change in the status of membrane technology was in the period from 1960 to 1980. Membrane formation processes, including interfacial polymerisation, multilayer composite casting, coating, and

membrane packaging methods such as spiral-wound, hollow-fine-fibre and plate-and-frame modules were developed for making high performance membranes. In 1980 the establishment of membrane processes, such as microfiltration, ultrafiltration, reverse osmosis and electrodialysis, meant these were installed in large commercial plants worldwide. The principal development in the 1980s was the development of industrial membrane gas separation processes. Nowadays, more and more engineered polymers are used to improve membrane performance especially solvent-resistant membranes. The market for membrane sales in 1998 was estimated at more than US \$4.4 billion worldwide, shared by different applications. 45% of the sales were in the United States, and 29% in Europe and the Middle East [28].

2.3.2 Classification of membrane processes

There are two main classifications of filtration processes; Dead-end and Cross-flow filtration as shown in Figure 2-1. In Dead-end (or in line filtration) the entire fluid flow is forced through the membrane under pressure, and any solid or colloidal particles accumulate on the membrane surface or in its interior to form a cake. Accumulation of solids on the surface can block the membrane pores, and the pressure required to maintain the required flow increases until a washing cycle is performed or the membrane must be replaced. The accumulation of suspended or dissolved substances on external surfaces, in pore openings, or within the pore structure of the membrane is known as membrane fouling, and this can result in severe reduction in permeability [34].

In the 1970s, an alternative process design known as cross-flow filtration was introduced. In a cross flow system, the fluid on the upstream side of the membrane moves parallel to the membrane surface, and the fluid on the downstream side of the membrane moves away from the membrane. This flow is circulated across the membrane surface producing two

streams, a clean permeate stream and concentrated retentate stream. Since the feed flow is circulated over the membrane, this creates a shear force on the surface, which reduces blocking of membrane pores on the surface of the material [35]. This flow type reduces membrane fouling; however, concentration polarisation, where the retained species become concentrated at the membrane surface, can occur with a solvent-particles system, as shown in Figure 2-2.

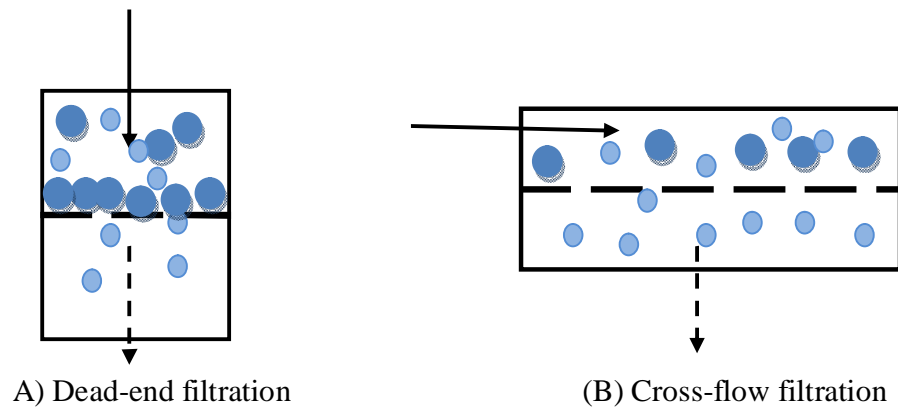


Figure 2-1 Dead-end and cross-flow filtration processes

Operating conditions and stream composition together create solute and/or particle concentrations near the membrane surface (concentration polarisation) that are significantly different to the bulk of the process stream. These dynamic surface conditions add more resistance to flow, which control the ultimate flux and selectivity of the system, and hence determine the final performance of a membrane system. Such an effect is controllable to some degree by employing a cross-flow filtration technique and optimising the hydrodynamic conditions above the membrane surface, often using mechanical vibration or ultrasound to disperse the solute away from the membrane surface [36-37]. The combination of bulk feed rate and feed path design contribute to the degree of polarisation, which impacts on both the flux and selectivity of the membrane.

Dead-end technology is usually used for batch operations, such as solid-liquid separations. While cross-flow can be used for similar separations, it is normally used in conjunction with continuous processes. The equipment required for cross-flow filtration is more complex, but the membrane lifetime can be much longer than in dead-end filtration.

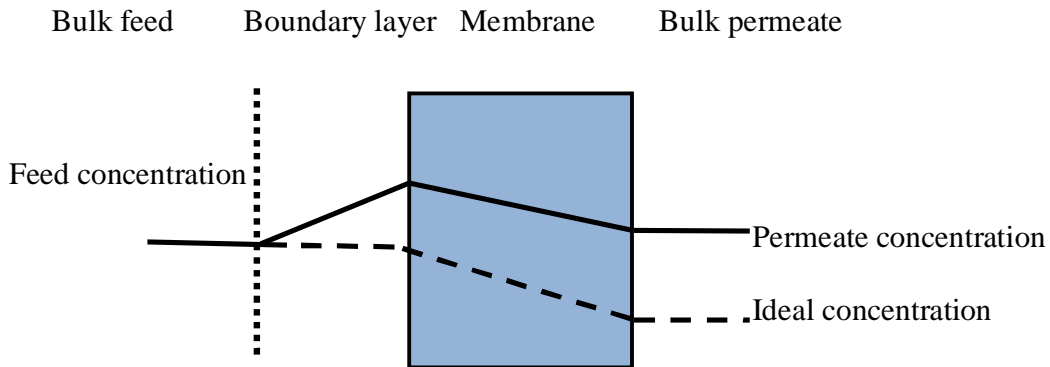


Figure 2-2 Effect of concentration polarisation on concentration profile for filtration

2.3.3 Classification of membranes

The wide range of membrane applications lead to six different classifications that are currently accepted: Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), Reverse Osmosis (RO), Pervaporation (PV), and Gas Separation. This classification is not absolute as there can be significant overlap between them. MF, UF, NF, and RO and their applications differ principally in the average pore diameter of the membrane as shown in Figure 2-3.

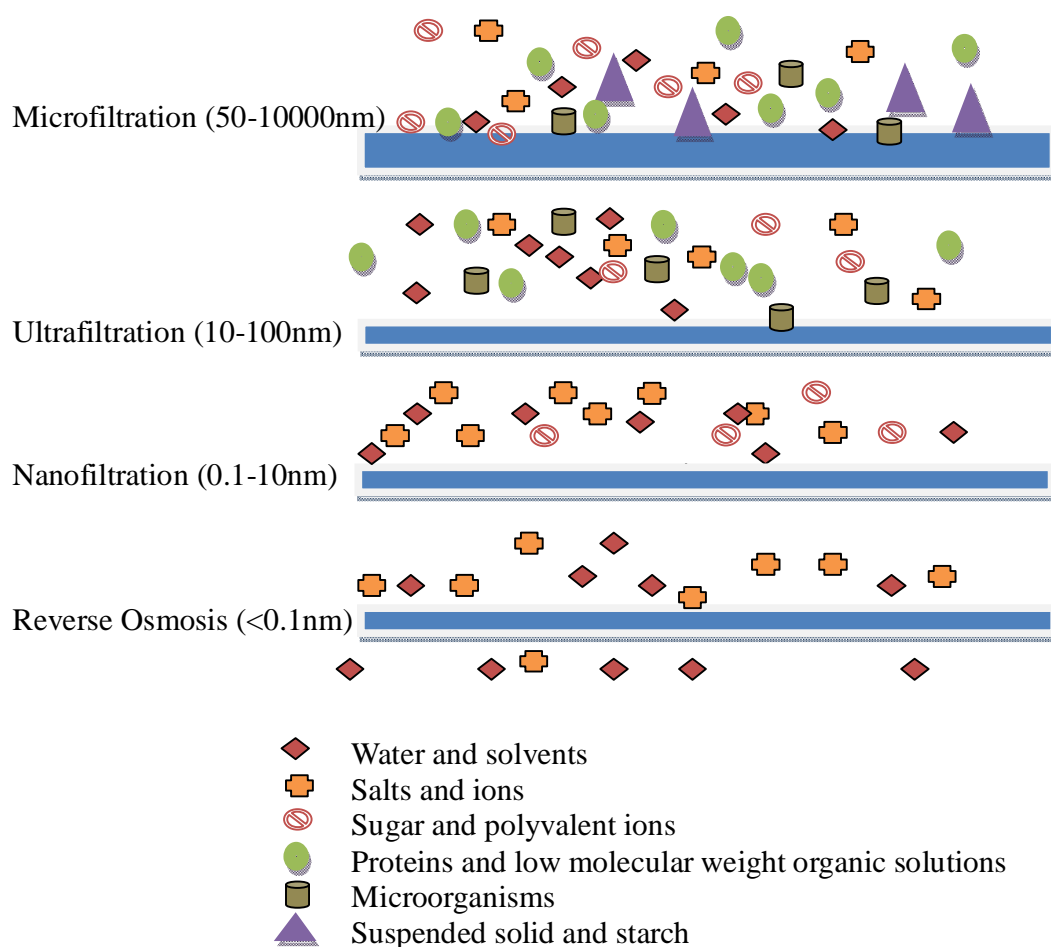


Figure 2-3 Membrane classifications and their application range

2.3.3.1 Microfiltration (MF)

Microfiltration (MF) refers to a filtration process that uses a porous membrane for the retention of suspended micron-sized particles. It is a pressure-driven separation process, and the separation process works primarily by size exclusion, permitting smaller species to pass through the membrane, while larger ones are retained. MF is used to retain colloidal particles, suspended solids and high molecular weight components. As a result several typical applications have been developed for MF technology: drinking water treatment,

filtration of various wastewaters for reuse, RO pre-treatment, biotechnology research and bio-processing, and chemical and water filtration in semiconductor fabrication. MF can be conducted using both Dead-end and Cross-flow filtration. The principal problem in MF applications is membrane fouling, which can be reduced by using Cross-flow or back washing [38-39].

2.3.3.2 Ultrafiltration (UF)

Ultrafiltration (UF) is a pressure-driven process with membrane pore sizes in the range of 10-500nm. UF separates the stream into two fractions on the basis of molecular size and charge. While UF and MF appear similar, they produce dramatic differences in the way the membranes are used, and have different applications based on their pore diameter. UF is used for protein separation and recovery of carbon black, as well as the removal of colour, which is present in some drinking water, and in separating colloidal suspensions, oil emulsions, viruses and protein material from solutions. UF membrane applications range from the treatment of industrial wastewater to the purification of drinking water, dairy processing, and the removal of macromolecules (proteins, polyphenols, polysaccharides, etc.) from water. UF in particular is an efficient technique for separating particles ranging from 10 nm up to a 500 nm from a liquid medium. In most applications of UF in industry, the principal problems inhibiting wider application of the technology are concentration polarization and fouling [40-41].

2.3.3.3 Nanofiltration (NF)

NF refers to filtration processes that have pore sizes ranging from 0.1 nm to 10 nm, and also dense membranes. With such a small pore size NF membrane are able to remove nanoparticles, certain salts and other dissolved substances. NF membranes have a typical operating pressure range from 5 to 20 bar, other research are showing that operating

pressure are up to 40 bar [28]. The NF system has wide applications in removing chemical and biological contaminants from aqueous streams such as monovalent and multivalent ions, and organic solutes with different size from one another. NF applications exist in the food industry, where the standards for food products are very high (e.g. dairy industry). Potential beneficiaries of nanofiltration applications in the food industry are low fat products, low calorie products and products suitable for special diets where NF can be used to separate carbohydrate and salts from food products. Pharmaceutical industries require the use of NF with liquid streams for removing biologically active organisms. NF membranes are seeing growing applications in the separation of ethanol, and recently the removal of trace amounts of volatile organic compounds from contaminated water. However, the fundamental behaviour of these membranes with organic solvent that can be translated into modelling and simulation tools is not well understood [42]. The drawbacks of NF in organic solvent filtration are the lack of membrane stability and relatively short membrane lifetime.

2.3.3.4 Reverse Osmosis (RO)

RO refers to a process where the applied pressure exceeds the osmotic pressure. RO membranes are generally considered to have no manufactured pore structures, but consist of a polymer network, in which solutes can be dissolved [43]. RO is based theoretically on osmosis phenomena, and pressure is required to overcome the osmotic pressure created by the difference in solute concentrations [44].

The first RO membrane which could be used at the industrial scale in water production plants was a cellulose-acetate-based membrane invented by Loeb and Sourirajan in 1960 [45]. This membrane was based on composite membrane structure having a very thin active layer on a coarse supporting layer. Fabrication of asymmetric flat-sheet membranes

elements using cellulose acetate allowed spiral wound membrane elements to be developed. RO technologies have been used commercially and in industry since 1964. The applications of RO are in seawater desalination, water makeup for industrial processes, and ultrapure water production in semiconductor industries [46]. RO and NF appear similar in concept and operation; however they produce dramatic differences in the way the membranes are applied. The difference between RO and NF is due to the membrane material, the operating conditions and transport mechanism. NF has the advantage of low operating pressure compared to RO, and higher molecule retentions compared to UF. The key difference is the retention of monovalent ions, such as chlorides. Reverse osmosis removes the monovalent ions at 98-99% level at 16 bar. NF membranes' removal of monovalent ions varies between 30 to 50% [47] depending on the material and manufacture of the membrane.

2.3.3.5 Pervaporation (PV)

PV is a membrane process in which the fractionation of a liquid mixture is obtained by a partial vaporisation of the mixture through a membrane to a vacuum chamber. It is a relatively new membrane separation process similar to RO and gas separation. However, unlike reverse osmosis and gas separation, PV involves a phase change. In PV a liquid mixture is absorbed at the membrane surface, and diffuses through the membrane network to reach the permeate side as vapour. This involves a phase change of permeating species from the liquid to vapour state [48]. The separation occurs by applying a reduced pressure on the permeate side to maintain the permeate vapour pressure lower than the pressure of the feed liquid. PV is commonly used for azeotropic and close-boiling point mixtures [49-50]. The major applications of PV are:

- Dehydration of organic solvents

- Removal of organic compounds from aqueous solutions
- Separation of anhydrous organic mixtures

2.3.3.6 Gas separation

Gas separation refers to separation of different gases based on their solubility and diffusivity properties. It emerged from the laboratory scale to become a rapidly-growing commercially-viable alternative to traditional gas separation processes, such as distillation. Gas separation has wide applications in industrial processes such as carbon dioxide separation from natural gas and nitrogen/oxygen separation. These applications represent only a small fraction of the potential applications in refineries and chemical industries. Gas separation is a pressure driven process, yet separation is based on solution diffusion theory (detailed description in Section 2.3.5). Gas at the high pressure side of the membrane dissolves and diffuses to the low pressure side. The first implementation of commercial polymeric membranes for gas separation was in 1980 [28]. In gas separation different membrane systems can be used to separate oxygen from air. Other types of membrane systems are used in the separation of Uranium 235 from Uranium 238 in the enrichment process to obtain enriched uranium for nuclear fuel used in nuclear reactors.

2.3.4 Membrane materials

The development of membrane materials has led to two classifications of membrane structure, symmetric and asymmetric porous membranes.

Symmetric membranes can be divided into two categories: porous and dense. Symmetric porous membranes show uniform pore sizes in their cross-section. Symmetric porous membranes have a rigid, highly voided structure with interconnected pores. Thus, retention of solutes by porous membranes is mainly a function of molecular size and pore

size distribution. In general, only molecules that differ in size can be separated by porous membranes. Most UF and MF systems use porous membranes to perform the separation.

Dense membranes are those in which manufactured pores do not exist, and transport occurs within the distribution of 'free volume' between the polymer chains. Dense membranes consist of a non-porous film through which molecules are transported by diffusion under the driving force of a chemical potential gradient. The separation of components of a mixture is related directly to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the non-porous film. Thus, dense membranes can separate solvents of similar size if their solubility in the membrane material differs significantly [28].

Asymmetric membrane structures consist of a thin surface layer supported on a much thicker, porous substructure. The layers are usually made from different materials. The surface layer controls the separation properties and permeation rates of the membrane, while the substructure functions as a mechanical support. Asymmetric membranes are layered structures in which the pore size or even the composition changes from the top surface to the bottom of the membrane as shown in Figure 2-4.

The membrane structure differs based on the membrane application; usually asymmetric membranes have a thin selective layer. The thinner the selective layer the higher the membrane flux. The advantages of the higher fluxes provided by asymmetric membranes are so great that almost all commercial processes use such membranes.

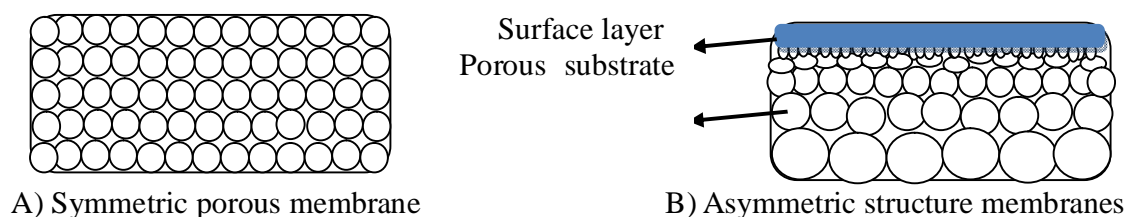


Figure 2-4 Schematic of the principal types of membranes structure

2.3.4.1 Polymeric membranes

Polymeric membranes have wide application as they can be made to a small thickness, and with a wide variety of pore sizes. Polymeric membranes can be classified as porous, e.g. MF or UF membranes, or as non-porous for example in NF, PV, and RO systems. The state of the polymer differs based on the membrane application. This is significant for mechanical, chemical, and thermal stability and has an influence on the permeation properties. Their state, whether amorphous or crystalline, means polymer membranes are generally classified into glassy, rubbery or elastomeric polymers. In the glassy state, the mobility of the polymer chains is very restricted, because the chains cannot rotate freely around their main chain bonds. The chain mobility and volume between the polymer chains, which is called the “free volume”, are responsible for the solubility and the diffusion of the molecules penetrating through the membrane [49].

The stability of the membrane is related to its ability to maintain both the permeability and selectivity under specific system conditions for an extended period of time. Stability is affected by the chemical, mechanical, and thermal properties of the membrane.

Improvements in membrane performance can be accomplished by modifying the polymer material by crosslinking. Crosslinking is the connection of polymer chains to form one network. Crosslinking changes the physical and chemical structure of the polymer, as the addition of more cross-linker to the polymer main chain changes the microstructure of the polymer network, making the polymer stronger and more rigid. Moreover, addition of more cross-linker reduces membrane free volume and changes membrane hydrophobicity/hydrophilicity. Polymer crosslinking therefore affects membrane performance and stability [51-52].

2.3.4.2 Ceramic membranes

Ceramic membranes have been developed from inorganic compounds, and have been used successfully for MF, UF, and NF in aqueous systems. Inorganic membranes have physical and chemical properties that are not shown by polymeric membranes, including better structural stability, and limited swelling or compaction. Generally, they resist severe chemical environments and high temperatures. These inorganic membranes can be broadly classified into five categories: glass, metal, carbon, ceramic and zeolite. These membranes are porous sieves, and separation is based on sorption-diffusion and size exclusion. Most inorganic membranes consist of alumina, Al_2O_3 as the support layer and a selective top layer [53]. Various studies have been carried out on different selective top layers such as silica, TiO_2 , ZrO_2 and zeolites.

Ceramic membranes are very resistant to a wide variety of solvents, and are stable in harsh operating conditions and a wide range of temperatures. Ceramic membranes are of interest in the field of waste treatment and pollution control because of their mechanical properties, chemical resistance, long working life and thermal stability [54]. These membranes also have potential use in molecular-sieving for gas separation, high-temperature gas-particulate separation, and a range of liquid separations [55-56].

2.3.4.3 Composite membranes

Developments in membrane materials witnessed the arrival of composite membranes in attempts to take advantage of specific organic/inorganic material properties. Composite membranes exhibit physical and chemical properties that are not, or only partially, shown by organic or inorganic membranes, including better structural and chemical stability. The majority of composite membranes proposed involve an inorganic-polymer composite, and rely on physical attachment of the polymer to the inorganic substrate via solution casting,

coating, and dip-coating of a porous ceramic substrate followed by subsequent crosslinking, or polymer grafting on ceramic substrate. The advantage gained by using a composite membrane is that each material can be optimised separately to provide improved membrane performance. Current research is focused on synthesis and fabrication of low cost membrane modules for high selectivity applications, and development of composite materials that can withstand the harsh chemical and physical environments required.

2.3.4.4 Solvent resistant membranes

The stability of polymeric membrane materials towards organic solvents is one of the key issues in solvent-resistant membrane development. Solvents may cause mechanical instability due to swelling, or can dissolve the polymer if not crosslinked. Alterations in the membrane performance or instability of polymeric membranes in organic solvents are not always noticeable. Even when there was no apparent interaction between membrane and solvent, membrane properties might have changed. Pore sizes may have changed, or the hydrophobic/hydrophilic character of the membranes may have shifted. Therefore membrane materials for organic separations must resist severe chemical environments [57].

Membranes can be made more stable by, e.g., increasing the degree of crosslinking of the polymeric top layer [58], by using alternative membrane materials [59], or by improving more common materials [60]. Composite membranes have been developed and have been used successfully for solvent-resistant membrane nanofiltration (SRNF) [57, 59-61]. SRNF has wide applications in petroleum processing to produce a cleaner gasoline, pharmaceutical engineering for separation of homogeneous organometallic catalysts, and recovery of hexane in the food industry [62].

2.3.5 Transport processes and mechanisms

The mass transfer of a substance through a membrane is a complex interaction between that substance and the membrane material. The transportation of a substance through a membrane can be broken down into five steps [63], which must be followed for the component to pass from feed to permeate, as shown in Figure 2-5.

1. Mass transfer from the feed bulk to the feed membrane interface.
2. Sorption from feed to membrane interface.
3. Transport through the membrane by diffusion (dense membrane) or by hydraulic flow (porous membrane).
4. Desorption at the membrane-permeate interface.
5. Mass transfer from the interface into the bulk permeates.

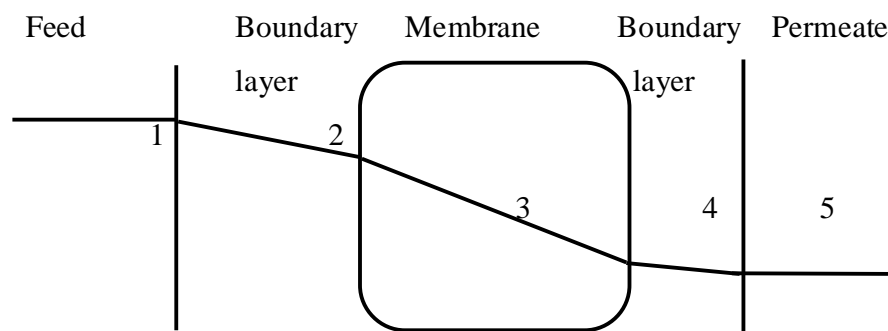


Figure 2-5 Transport through a membrane

According to this mechanism, permeation consists of five consecutive steps; each of these represents a resistance that a substance must overcome. If any of these resistances is significantly higher than the rest, it will be the rate-determining step. The resistance of the other steps can be neglected so that the mass transfer in these regions is instantaneous compared to the rate determining step. The driving forces behind the transportation

process are concentration and pressure, which can be combined as the difference in the chemical potential across the membrane. Studies by Robinson *et al.* [64], Sharma *et al.* [65], and Manjula *et al.* [66] suggested that sorption and diffusion are the principal rate-determining steps, and these depend on the solvent-polymer system.

2.3.5.1 Mass transfer models

The transportation of molecules in a membrane can be classified into two categories: physical transportation and chemical transportation.

Physical transportation processes assume that solvent and solute flow through a pore within the membrane material, and are based on hydraulic transport. The flux can be described by viscous flow through membrane pores. It is still not clear whether transport through a dense membrane (both solvent and solute) occurs by viscous flow or diffusion. Paul *et al.* [67] suggested that solvent viscosity has a major role in the transport through membranes. Robinson *et al.* [64] assumed viscous transport through a dense polydimethylsiloxane (PDMS) to correlate the permeability of various alkanes. They indicated that PDMS has no defined porous structure, but the membrane behaves as if it has pores, which in turn infers a hydraulic transport mechanism. Yang *et al.* [68] showed that viscous flow could not explain their measurements. They suggested that membrane swelling in the presence of organic solvents caused the deviation from viscous flow model. Chemical transportation takes into considerations the interaction between that substance and the membrane material. Studies by Paul and Ebra-Lima [69] attempted to model the diffusion of organic liquids through swollen polymeric membranes. They concluded that highly swollen membranes can yield very high liquid flux at moderate pressure and consequently may have application for performing certain separations. This assumption was presented by Ten and Field [70], who presented mass transfer models for

pervaporation of organics from water. They found that sorption and desorption kinetics were orders of magnitude higher than the other transport steps, and were influenced by solvent membrane interactions. Machado *et al.* [71] introduced the resistance-in-series model, which relates the flux of a solvent mixture with easily measurable solvent and membrane properties (surface tension, viscosity and membrane hydrophobicity). Their model did not include the swelling effect. Bhanushali *et al.* [72] developed a permeation model for hydrophobic membranes, which uses the molar volume and viscosity of the solvent as parameters for predicting the pure solvent permeability. They found that polymer-solvent interactions are critical towards the development of suitable materials and also the prediction of the transport mechanisms. Geens *et al.* [73] introduced a new model based on the viscous flow model, Machado model and Bhanushali model. The newly developed model introduces a correction to account for the solvent-sorption parameter. They suggested that solvent flux appears to be dependent on viscosity, molecular size and the difference in surface tension between the membrane and the solvent. The literatures conclude that the permeation of a substance through a dense membrane is a complex interaction between that substance and the membrane material, and cannot be explained by a simple permeation model. It should be noted that the complexity of the models increases dramatically for multi-component systems which require the use of more thermodynamic data to correlate the permeability of various component through membrane systems.

2.3.5.2 Pore flow model

The pore flow model is based on the physical transport process, in which permeate is separated by pressure-driven convective flow through pores, such as in MF and UF. The pore flow membrane model supposes that pressure forces a liquid through a semi-permeable membrane. Suspended solids and solutes of high molecular weight cannot pass

through membrane pores, and are rejected, while water and low molecular weight solutes pass through the pore volume. Separation occurs because one or more of the substances is excluded from some of the pores through which the other substances pass as shown in Figure 2-6.

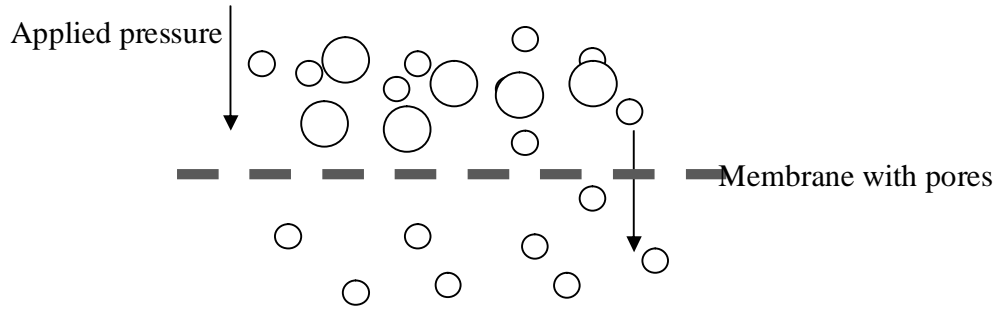


Figure 2-6 The transportation mechanism of mixtures based on the pore flow model

According to Darcy's Law, physical transport through membranes and other porous media is a pressure driven. Darcy's Law is expressed by Equation 2.1 [74]:

$$J = B \frac{\Delta P}{l} \quad (2.1)$$

Where J is the total flux (m/s), B is the permeability coefficient, which includes the viscosity term ($\text{m}^2/\text{s} \cdot \text{bar}$), ΔP is the pressure difference, and l is membrane thickness. In the case of a porous membrane, pressure is the driving force for solvent transport through the membrane. The pore flow model assumes the pressure difference produces a smooth pressure gradient through the membrane. However, the solvent concentration remains constant within the membrane and the difference between solvent concentration in liquid and corresponding solvent concentration within membrane is due to sorption and desorption at the membrane surface as shown in Figure 2-7 (adapted from [74]).

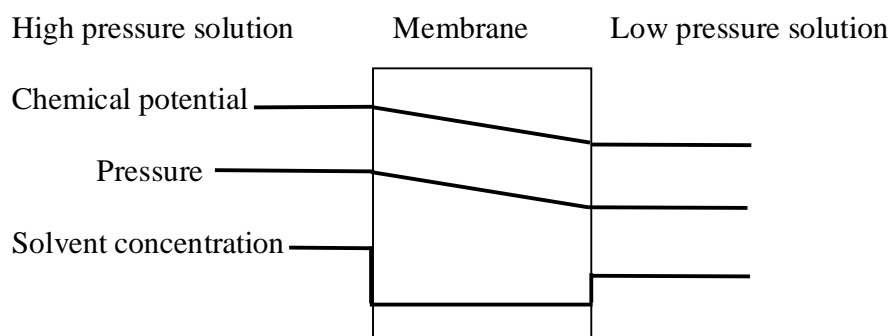


Figure 2-7 Transport of a component through a membrane according to the pore flow model

The pore flow model cannot explain transportation in some filtration processes, such as gas separation, because the pore flow model is closer to physical transport. The NF process generated much debate as to whether it is described by pore flow because permeation and rejection is influenced by solvent size and membrane pore size. In the case of dense membranes the pore flow model considers that the membrane behaves as if it has an appreciable free volume through which viscous permeation takes place. Van der Bruggen *et al.* [57] and Geens *et al.* [73] suggested that NF could be described by such a mechanism. However, the interaction between the solvent and membrane may cause polymer swelling and deviation from pore flow model [68]. The limitations of the pore flow model are the factor behind the development of the solution diffusion model.

2.3.5.3 Solution diffusion model

The solution diffusion model is based on the chemical transport process, in which a substance dissolves in the membrane material, and then diffuses through it. Separation occurs due to the differences in the amount of material that dissolves in the membrane, and the rate at which the material diffuses through the membrane. Permeation is strongly

influenced by the affinity of the membrane towards one or more components in the feed, and the ease of diffusion of the permeating molecules through the membrane matrix.

The solution diffusion model assumes that when a pressure is applied across the membrane, the pressure remains constant within the membrane material. Consequently, the pressure difference across the membrane produces concentration gradient within the membrane and the difference between solvent concentration in liquid and corresponding solvent concentration within membrane is due to sorption and desorption at membrane surface, as shown in Figure 2-8 (adapted from [74]). The diffusion can be described by Fick's law according to Equation 2.2.

$$J_i = D \left(\frac{dc_i}{dx} \right) \quad (2.2)$$

Where J is the total flux (m/s), $\left(\frac{dc_i}{dx} \right)$ is the concentration gradient and D is the diffusion coefficient.

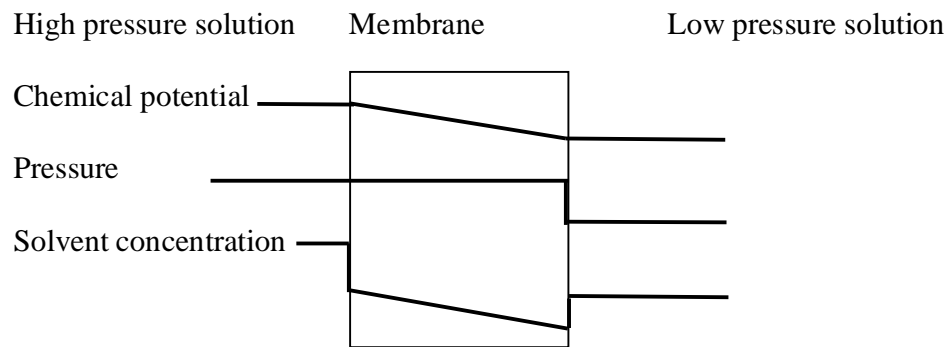


Figure 2-8 Transport of a component through a membrane according to the solution diffusion model

The solution diffusion model and pore flow models differ in the way pressure and concentration gradients are expressed. The solution diffusion model assumes constant pressure within the membrane, while the pore flow assumes constant concentration within the membrane. However, the solution diffusion model assumes concentration gradient

within the membrane, while pore flow assumes a pressure gradient through the membrane. The solution diffusion model is applicable to different filtration processes, such as PV, and gas separation. The applicability of solution diffusion and pore flow model to NF has been a subject of debate, with both models providing an adequate explanation for some experimental observations in NF. Gibbins *et al.* [75] suggested that the pore flow model is favourable in describing the increase solute rejection with increasing pressure due to hydraulic flow. However the solution diffusion approach was used by Mulder *et al.* [76], who investigated separation of ethanol/water by cellulose acetate membrane and suggested that permeation takes place by a substance dissolving in the membrane material and subsequently diffusing through it. They concluded that selectivity of the membrane is governed by differences in the solubility and diffusivity of the permeating species. Vankelecom *et al.* [77] used PDMS membrane in solvent extraction and suggested that solution diffusion type models may be more appropriate than pore flow models for describing transport of solvents through this membrane. However, Wijmans and Baker [74] suggested that both mechanisms can occur based on the existence of diffusion and pores-like region within membrane.

2.3.6 Separation mechanisms

The separation mechanisms by membranes are influenced by both membrane characteristics and the properties of the solvents and solutes. Solvent properties, such as molecular size and polarity and membrane properties, such as pore size, charge and hydrophobicity/hydrophilicity influence membrane selectivity.

2.3.6.1 Separation based on size

The difference in pore diameter produces dramatic differences in the application of MF, UF and NF membranes. These separation processes are pressure-driven, based on

membrane pore size and the molecular diameter of suspended material and the pH of the solution (for aqueous streams). When the molecules are larger than the membrane pores, rejection of the molecules occur as a result of size exclusion (sieve effect). Membranes are usually quantified by their nominal molecular weight cut-off (MWCO), which is the smallest molecular weight species for which the membrane has more than 90% retention. In these separation processes the molecular weight is recognised as a useful descriptor of the membrane selectivity. Kiso *et al.* [78] reviewed the molecular width and radius of more than 36 organic compounds in order to examine the effect of molecular shapes on the separation of organic solute through a cellulose acetate RO membrane. They found that the selectivity was affected by molecular size, molecular structure and orientation of the organic solute in the pore. The solute orientations are controlled by the interaction between the solute and membrane material. Robinson *et al.* [79] evaluated the rejection of organic compounds using a PDMS membrane based on the molecular size. They suggested that the rejection mechanism for organic solutes is shown to occur via size exclusion, with the rejection also being dependent on the degree of membrane crosslinking. Agenson *et al.* [80] combined molecular width and molecular length with hydrophobicity to predict the rejection of organic compounds. They indicated that a higher rejection was obtained for a more hydrophobic molecule with a larger width and length. Van Baelen *et al.* [81] performed experiments with methanol-water, ethanol-water, isopropanol-water and acetic-water mixtures to investigate the influence of molecular size and polarity on the rejection behaviour. They explained that NF combines molecular size with charge effects between solution and the membrane. They suggested that the rejection of uncharged (organic) molecules is determined by the size of the dissolved molecules compared to the size of the membrane pores.

2.3.6.2 Separation based on charge and polarity

Membrane charge plays a significant role in rejection mechanisms, as the exclusion or permeation of polar or charged components may be a result of the attractive or repulsive force generated between the component and membrane in both aqueous and non-aqueous systems. Separation can be based on the exclusion of solvents having the same charge as those fixed on the membrane structure, where repulsive interaction exists. This was observed by Zhao *et al.* [82] who investigated rejection of charged and neutral molecules in some solvents such as water, water–methanol, methanol, ethanol, acetone and ethyl acetate. They observed that the rejection of charged molecules is higher in water than in organic solvents and rejection of neutral molecules in water is higher than in organic solvents for hydrophilic NF membranes. They suggested that the rejection mechanisms are dependent on the molecular charge and solvent polarity.

Solvent polarity can be defined as these molecules that have permanent dipole moments such as water, while molecules in which all the dipoles cancel out (zero dipole moment) are said to be non-polar, such as heptane. Van der Bruggen *et al.* [83] studied the polarity of the solvents such as water, ethanol, and n-hexane on the rejection mechanism in NF. They showed that rejection increased with decreasing solvent polarity with hydrophobic membranes; however, rejection decreased with decreasing polarity for hydrophilic membranes. Burshe *et al.* [84] studied the effect of polarity of water, methanol, ethanol, isopropanol, and n-butanol on rejection mechanisms. They found that rejection increased with increasing polarity of solvent. Tarleton *et al.* [85] investigated the influence of polarity on rejection behaviour, and concluded that rejection of polar components depended on their concentration in the feed mixture, while the extent of rejection was also dependent on polarity.

2.4 Methods to quantify membrane selectivity

Two different types of selectivities are defined for a membrane: ideal selectivity and actual selectivity. The ideal selectivity is defined as the ratio of fluxes of pure substances through the membrane, and the actual selectivity (α) of a membrane in a binary system is defined as the concentration ratio of the components in the permeate and in the feed mixture.

$$\alpha = \frac{(Y_1/Y_2)}{(X_1/X_2)} \quad (2.3)$$

where Y and X are the weight fraction of component in permeate and feed respectively and 1 and 2 subscripts denote the two components to be separated. The overall selectivity of a membrane is influenced by sorption of one or more components into the membrane, and the ease of diffusion of the permeating molecules. The selectivity of a membrane is mainly governed by the sorption of component into the membrane rather than diffusion [86].

2.4.1 Factors affecting membrane selectivity

Membrane selectivity is greatly impacted by the process operating conditions, the stream nature and the chemical composition of the process [87-88]. Operating conditions such as pressure, temperature, and flow rate [89-90], stream composition [91-92] and the membrane material properties [93-94] all control the selectivity of the membrane system. The membrane selectivity is also determined by less obvious material properties such as material morphology, for example degree of crosslinking [95], polymer composition [96-99], hydrophobicity/hydrophilicity [96-97, 100-102] and membrane surface charge [96-97, 103]. The results of a wide range of experimental studies conclude that selectivity varies with many parameters, so it is important to report the selectivity data range for different membrane materials, rather than quote a single value [42] (details in Section 2.4.2).

2.4.2 Membrane performance data

Membrane performance is characterised by permeability and selectivity. The following Table 1.1 and Figure 2-9 review permeability and selectivity data for alcohol/water from different literature sources using different membranes.

The permeability coefficient as defined in Equation 2.1 was calculated based on the flux of alcohol per unit pressure over temperature range from 20-80 °C, the viscosity incorporated within permeability coefficient, and selectivity is the concentration ratio of the components in permeate and feed mixture as defined in Equation 2.3. The thickness of the active separating layer was not reported in most of the literature as the membrane permeability to alcohol is inversely proportional to its thickness [104], therefore the data is limited in terms of membrane thickness. The results are shown in Table 2.1 and average alcohol permeability versus average alcohol selectivity values for different membrane materials are presented in Figure 2-9.

CHAPTER TWO LITERATURE REVIEW

Table 2.1. Permeability coefficient and alcohol selectivity of membranes for alcohol/water

Material	Permeability coefficient (B) g/h.bar	Selectivity (α)	Operating conditions		References
			Alcohol concentration wt%	T, °C	
PVA	70-2500	45-410	10-90	45-60	[105-112]
Chitosane	33-472	77-1400	10-90	25-60	[113-124]
Alginate	90-500	16-1200	10-90	30-50	[125-132]
Polysulfone(PSF)	173-600	240-1000	10-90	25-40	[133-138]
Polyimides	130-890	5-900	10-90	25-75	[139-144]
Polyamides	140-350	4-1305	10-90	20-25	[145-146]
Polyelectrolyte (nafion)	300-1100	50-600	10-90	25-50	[147-151]
Polyaniline	300-1200	212-564	10-90	25-80	[152-155]
Mixed polymer (PVA/clay)	50-280	30-1600	3.5-96.5	20-40	[156-159]
PDMS	14-130	120-2400	5-10	25-60	[160-169]

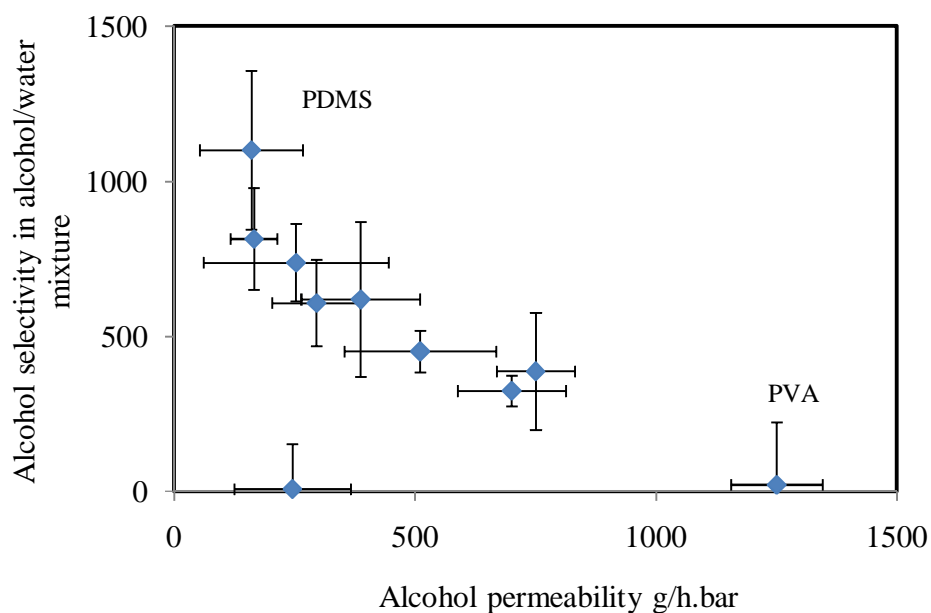


Figure 2-9 Alcohol permeability and selectivity

The results illustrate the selectivity of membranes towards alcohol published by different workers, based on Table 2.1. PDMS and PVA are labelled as they represent the two extreme examples of the permeability/selectivity relationship. The data in Table 2.1 shows that from PVA to PDMS, the selectivity increase and the permeability decrease.

Results in Figure 2-9 show that membranes with high permeability tend to show low selectivity. Unfortunately, polymeric membranes typically display a permeability-selectivity trade off, i.e. permeability typically varies inversely with selectivity. Thus, membranes with desirable permeability often do not have a desirable selectivity. In addition, both selectivity and permeability of most membranes is a strong function of the feed composition and temperature.

Polymeric PDMS and PVA membranes were found to exhibit the highest selectivity and the highest permeability respectively. A similar result was observed by Chapman *et al.* [170] who suggested the use of a pervaporation separation index (PSI), which is the multiple of selectivity and flux. However, the PSI fails to distinguish the overall membrane performance, since a membrane with low separation factor and high flux can have the same PSI as one with high separation factor and low flux. This indicates that selecting the membrane with highest PSI may not always be the optimum choice for the process. The selectivity of PVA and PDMS in alcohol/water mixtures will form the basis of the work within this thesis, as these materials represent two extremes of performance.

2.4.3 Organic/organic systems

The most widely encountered organic/organic systems exist in the petrochemical industry, which deals with a large number of organic mixtures. The major separations of organic mixtures can be categorised into the following [171]:

1. Separation of polar/non-polar solvent mixtures, such as ethanol/hexane

2. Separation of aromatic/cyclic mixtures, such as benzene/heptane
3. Separation of aromatic/aliphatic hydrocarbons, such as toluene/cyclohexane
4. Separation of isomers, such as n-hexane/cyclohexane

This review considers the separation of polar/non-polar mixtures, such as ethanol/hexane and ethanol/heptane, which are used as model examples for separation. Due to their extreme polarity difference they are used as model systems, which can be used to gather the necessary mechanistic understanding, before consideration of the more relevant but more challenging alcohol/water systems.

Tarleton *et al.* [172-173] used PDMS as NF membrane for solute removal from liquid hydrocarbons. They suggested that solvent polarity plays a significant role in determining levels of flux and rejection. They concluded that rejection was dependent on trans-membrane pressure, cross flow rate, solute size and the mixture polarity. The same workers used PDMS for selective solute removal from fuels and solvents. Farid and Robinson [174] used different concentration of ethanol/hexane and ethanol/heptane to study the effect of polarity on the separation mechanism in PDMS membranes. They concluded that PDMS transfers from being ethanol selective at low ethanol concentration to be hexane/heptane selective with increasing ethanol concentrations.

Stafie *et al.* [175] studied the transport of hexane-solute systems through PDMS composite membranes in the food industry. They found that the degree of PDMS crosslinking in conjunction with the polarity could be used to describe the aspects of transportation of such systems. They indicated that hexane rejection increases with increasing degree of crosslinking and indicated that the ethanol rejection is based on the polarity of the mixture. Stamatialis *et al.* [176] studied the rejection of ethanol/hexane in different crosslinked PDMS membranes. They suggested that polarity difference could explain the separation

behaviour, and concluded that a linear relationship exists between the solvent rejection and membrane crosslinking.

2.5 Key criteria for membrane selection

The selection of material for organic separation requires the matching of performance characteristics of the material available with the application. Currently, there is no well-established criterion for the selection of membrane materials, and the materials for membranes process are normally selected empirically. Polymers with high selectivity are often preferred for further study because the disadvantage associated with low permeability can be partly compensated by improving the membrane structure, i.e. reducing the effective thickness of the membrane hence increase permeability [177]. For any membrane system, the material selection criteria must take into consideration membrane synthesis, structures, hydrophilicity/hydrophobicity, and membrane-solvent interaction.

2.5.1 Hydrophilicity/hydrophobicity and surface characterisation

The selection of materials for organic separation is based on the hydrophilicity and hydrophobicity of the membrane. The need to define the hydrophilicity and hydrophobicity of the membrane is essential to characterise membrane performance, and previous literature attempted to correlate the performance based on hydrophilicity and hydrophobicity. Braeken *et al.* [178] investigated the influence of molecular size, hydrophobicity, and adsorption of dissolved organic compounds in aqueous solutions. They found good correlation between organic hydrophobicity and selectivity. Their results showed that molecules with high hydrophobicity, generally, had low selectivity, while molecules with a low hydrophilicity showed high selectivity. Bhanushali *et al.* [72, 179]

studied a range of solvents and solutes with both hydrophilic and hydrophobic membranes. They proposed a model for predicting the pure solvent permeation through hydrophobic polymeric membranes. However, Van der Bruggen *et al.* [180] analysed solvent flux in different membranes by a model which considered the hydrophobicity/hydrophilicity of the material. They suggested that changes in the membrane structure cause a change in hydrophobicity or hydrophilicity. Geens *et al.* [181] studied raffinose in water and raffinose in methanol with hydrophobic and hydrophilic membranes. They found higher rejection of raffinose in methanol than in water for a hydrophobic membrane compared with a lower rejection with a hydrophilic membrane. They suggested that, for hydrophobic membranes, the affinity to water molecules is very low and water contact with the membrane is almost non-existent. However the affinity of hydrophobic membrane with methanol molecules is high, leading to higher rejection in methanol than in water.

Thus, the conclusion from this literature is that polymer materials for alcohol dehydration should have a suitable hydrophilicity. Hydrophilic polymeric membranes preferentially absorb the water molecules over other molecules in the process stream. For example, membranes with low hydrophilicity, such as PDMS, generally exhibits low water selectivity in dehydration, but some membranes made of polymers with very high hydrophilicity, such as PVA, permeate water selectively.

2.5.2 Membrane swelling

Swelling is an important criteria in the selection of a membrane for organic separation. Membrane swelling plays a key role in the transport of molecules through membranes, as swelling changes the physical and chemical structure of the polymer. The greater the affinity between solvent and polymer, the more polymer swelling occurs. Swelling of dense polymers leads to an increase in the free volume. The membrane becomes more

open and allows more liquid to move through, which influences both permeability and selectivity. However swelling of porous membranes leads to contraction of the pores walls and pores becoming more narrow, which enhances selectivity but decreases permeability [182].

Membrane swelling characteristics have an impact on membrane rejection, which occurs through several mechanisms:

- Size exclusion: molecules are too large to enter the transport region within the membrane.
- Surface repulsion: molecules can be repelled due to hydrophobic/hydrophilic interactions with membrane materials or electrostatic forces.
- Adsorption: the membrane surface absorbs one or more molecules of the permeate selectively.

Rejection is not governed by a single mechanism but it is a contribution of different mechanisms. It is postulated that the membrane swells, the polymer chains are stretched and the free volume in the space between them increases hence increasing solvent permeability [183]. Researchers examined the swelling of many different NF membranes with several species, in both aqueous and non-aqueous systems. Tarleton *et al.* [183] observed NF membrane swelling with organic solvents, such as methanol, ethanol, propanol, and n-heptanes. They postulated that swelling increases the free volume within the membrane, which can be interpreted as an induced pore-like structure or raised membrane porosity. They suggested that poor-swelling solvents yield a lower flux and higher solute rejection than good-swelling solvents. They conclude that the degree of polymer swelling governs the transport regions within the membrane, and hence, the overall solvent flux and solute rejection characteristics. Robinson *et al.* [64] examined flux

of organic solvents through PDMS membrane for *n*-alkanes, *i*-alkanes and cyclic compounds. They showed that swelling is a good indicator of permeation. Due to swelling, so-called channels are formed and the solvent flux increases. Verhoef *et al.* [182] investigated pervaporation of ethanol/water mixtures through a hydrophobic membrane. They suggested that the difference between NF and pervaporation membranes is explained by the influence of swelling, and the different interactions between permeating molecules and the membrane. Mohammadi *et al.* [184] measured the swelling degree of PDMS in alcohol/water binary mixtures as a function of alcohol concentration. They showed that the swelling degree of PDMS in ethanol/water is higher than the swelling degree in methanol/water, and concluded that selectivity of a membrane is mainly governed by the sorption component. Yeom *et al.* [185] used the degree of PVA swelling to assess the membrane selectivity in ethanol/water mixture. In the case of a highly swollen membrane, the membrane pores influenced and hence transport through the membranes. Farid and Robinson [186] studied removal of alcohols (ethanol and isopropanol) from water using PDMS as an example of hydrophobic material, and concluded that a non linear relation existed between sorption and alcohol concentration in the swollen polymer. These literatures conclude that swelling is an important factor, as it affects permeability and selectivity. In this work, polymer swelling in solvent mixture is used to assess the solvent-polymer interaction, and hence membrane selectivity.

2.5.3 Solubility parameters

The component solubility in the membrane depends primarily on the affinity of those molecules towards the membrane material. This affinity can be quantified using the solubility parameter of each material rather than using qualitative such as terms hydrophobicity and hydrophilicity. The solubility parameter is a numerical value derived

from the cohesive energy density of the solvent, which in turn is derived from the heat of vaporisation. Since the solubility of two materials is only possible when their intermolecular attractive forces are similar, one might also expect that materials with similar cohesive energy density values would be miscible. In 1936, Hildebrand [187] proposed the square root of the cohesive energy density as a numerical value indicating the solvency behaviour of a specific solvent.

$$\delta = \left(\frac{\Delta E}{V} \right)^{1/2} \quad (2.4)$$

where ΔE is the cohesive energy, V is the molar volume. Hildebrand solubility parameter (δ) can be adequately used in many cases to describe solubility behaviour [188]. However, in some cases, δ does not give accurate results due to the presence of polar components. Hansen [189] suggested the combination of all three polar forces (hydrogen bonding, polar forces, and dispersion forces) at the same time to give greater accuracy. The Hansen solubility parameter is a measure of the total energy required to liberate molecules from forces that hold the molecules together in the liquid phase. These forces are dispersion forces, polar interaction, and the energy needed to break hydrogen bonds, as indicated by Equation 2.5.

$$\delta = \sqrt{\delta_d^2 + \delta_r^2 + \delta_h^2} \quad (2.5)$$

where δ_r is polar interaction, δ_h represents hydrogen bonding and δ_d represents dispersion forces. Equation 2.5 shows that the value of the solubility parameter is the sum of contributions using the numerical values assigned to the various structural groups. The units for δ can be expressed as the square root of the cohesive energy density ($\text{cal}^{1/2} \text{cm}^{-3/2}$) or as the square root of a pressure ($\text{MPa}^{0.5}$). Barton [190] reported solubility parameter values for a wide range of solvents and materials. Solvents having solubility values similar

to that of polymers would be expected to completely dissolve the polymer if it is not sufficiently crosslinked, whilst those with dissimilar values would not. The swelling behaviour of a polymer in a solvent could be predicted using the solubility parameter without knowing any other information about the solvent [191].

Similar solubility parameters indicate good compatibility of polymer and solvent. When polymer and solvent are mixed together, the enthalpy change of mixing (ΔH_m) can be expressed by the empirical correlation of the Hildebrand-Scatchard Equation 2.6 [192]:

$$\Delta H_m = V_m (\delta_p - \delta_s)^2 \Phi_p \Phi_s \quad (2.6)$$

Where V_m is the molar volume of the mixture, δ_s and δ_p are the solubility parameters of solvent and polymer respectively, Φ_p and Φ_s are the volume fraction for polymer and solvent in the mixture. For two components to be soluble in one another (i.e. for swelling to occur in a polymer-solvent system), the change in Gibbs free energy of mixing must be favourable, that is $\Delta G_m < 0$. The greater the magnitude of ΔG_m the more mixing is likely to occur. The free energy of mixing is related to the enthalpy change of mixing according to Equation 2.7.

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad (2.7)$$

where ΔS_m is the entropy change of mixing and T is the temperature at which the mixing occurs. The entropy of mixing is always positive (due to the increase in disorder upon mixing). A reduced enthalpy of mixing must be obtained, if substances are miscible, hence swelling is maximal when $(\delta_p - \delta_s)$ is 0 [193].

Yamaguchi *et al.* [194] used the same approach to quantify the swelling degree of polymers in different solvents. Bueche *et al.* [195] reported the swelling of a crosslinked PDMS in a number of swelling agents. They found the magnitude of the solubility parameter of the polymer depends markedly on the solubility parameter of swelling agents.

In addition, the solubility parameter could be used to predict separation in a ternary system (i.e. one polymer, p, and two solvents, s_1 and s_2). For example a mixture of A and B, where A is present in a very low amount and is to be separated; component A should have a solubility parameter close to the solubility parameter of the membrane material. This was observed by Lloyd and Meluch [196] who used the solubility ratio between permeate components, A and B, through the membrane, as a measure of preferential sorption for A and B in the membrane. For example, if component B is desired to permeate and component A is to be rejected, then membrane material should be selected to maximise the ratio δ_A/δ_B .

2.6 Polymer swelling

2.6.1 Swelling mechanisms

Swelling is a thermodynamic phenomenon, which can be considered as the mixing of a polymer and solvent, resulting in deformation of the polymer network [197]. The thermodynamics of liquid mixtures can therefore be extended to swollen polymers.

Yoo *et al.* [198] explained swelling equilibria in PDMS using a swelling model [199-200], which defines swelling equilibrium as the change in chemical potential of the solvent in the bulk phase, and the elastic deformation of the polymer network. When polymers are swelled in solvent at constant temperature and pressure, the change in chemical potential of components can be thermodynamically expressed as follows:

$$\Delta\mu = \Delta\mu_{mix} + \Delta\mu_{el} \quad (2.8)$$

Where $\Delta\mu_{mix}$ is change in chemical potential due to solvent polymer mixing; $\Delta\mu_{el}$ is the change in chemical potential due to elastic deformation induced by an expansion of the network structure. The elastic contributions were studied by Suwandi and Stern [201] for

crosslinked PDMS in different hydrocarbons, and concluded that the elastic contribution induced a negligible modification to polymer solvent mixing. The change in chemical potential due to solvent/polymer mixing can be expressed by:

$$\Delta\mu_{mix} = \mu_{ip} - \mu_{is} \quad (2.9)$$

$$\Delta\mu_{mix} = RT \ln a_{is} \quad (2.10)$$

where μ_{ip} and μ_{is} are the chemical potential of solvent in polymer and chemical potential of solvent in liquid respectively, and (a_{is}) is solvent activity within the polymer. The activity is the effective concentration of species in the mixture, since then it is used to understand, predict, and describe the sorption behaviour of a substance in a polymer solvent mixture [202]. For an ideal mixture, the solvent activity is expressed by the following equation:

$$a_{is} = C_{is} \quad (2.11)$$

where C_{is} is the mole fraction. For non-ideal mixtures the solvent activity may be derived from thermodynamic relationships, such as the Flory-Huggins theory (details in Section 2.6.3). The mechanism of swelling can be visualised as a combination of three distinct processes, as shown in Figure 2-10.

1. The solvent is absorbed at the polymer surface.
2. The solution penetrates into the polymer, first to occupy the free volume and then the solvent molecules diffuse into the polymer.
3. The polymer structure expands as the trapped solution in the pores next penetrates into the network of the polymer chains to swell them.

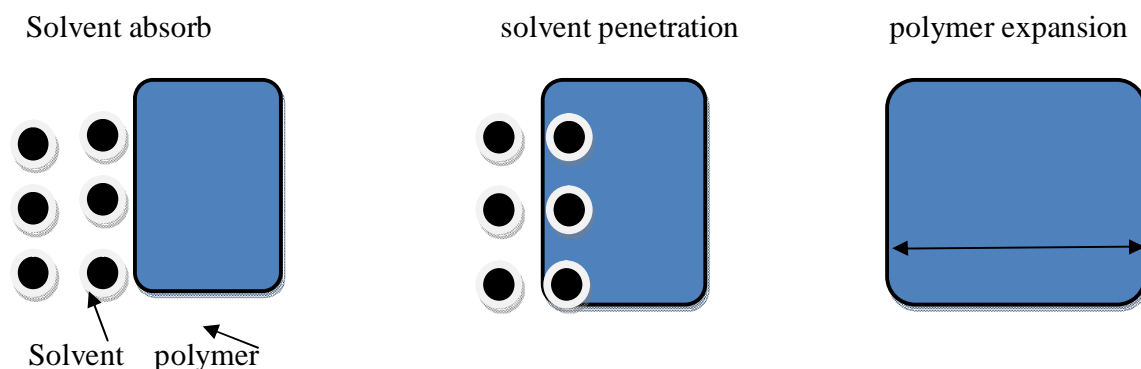


Figure 2-10 Polymer and solvent swelling mechanism absorption, penetration and expansion

There are two scenarios by which swelling can influence transport through a membrane. The first is the expansion of membrane free volume, hence letting larger molecules pass, increasing permeability and reducing selectivity. The second is compaction of membrane pores leading to an increase in selectivity and reduction in permeability. These two mechanisms could occur based on swelling as shown in Figure 2.11. Besides the molecular size, the molecule charge is another important parameter affecting separation in aqueous processes. When the molecular size is much smaller than the membrane pores, the molecular charge can be the decisive factor in determining rejection of the molecule [203].

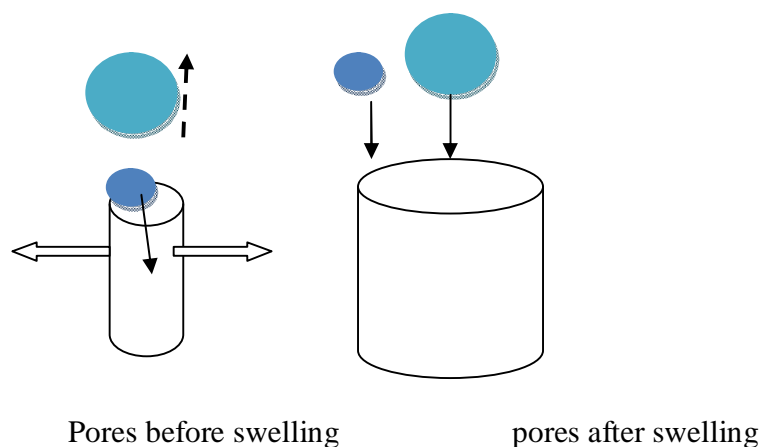


Figure 2-11 Swelling mechanism of membrane pore and rejection mechanism.

The influence of swelling also was argued by Ebert *et al.* [204] They suggested that in dense membranes polymeric chains move further apart during swelling and lead to lower rejections. Van der Bruggen *et al.* [57] demonstrated this assumption by SEM images for MPF-44 and MPF-50 membranes and indicated increase in membrane free volume during swelling process.

2.6.2 Swelling equilibrium and membrane selectivity

Consider a mixture of two solvents, one swells the polymer and the other does not. In this case it is expected that polymer swelling will be due to the existence of the highly swelling component in the mixture. Thus membrane swelling, as a result of interaction between the solvent and the polymer, is a determining factor in membrane selectivity. In Section 2.3.4.1 the effect of membrane micro-structure on membrane transports properties was indentified. Polymer preparation conditions, such as the degree of polymer crosslinking, will influence the swelling of the polymer and hence the selectivity. Nguyen *et al.* [205] prepared PDMS of different crosslinking content for pervaporation of water/ ethyl acetate mixtures. They indicated that due to swelling of PDMS, the polymer chains move further apart and allow more liquid to penetrate the polymer matrix. They indicated that PDMS selectivity to ester in the mixtures is lower than that in sorption ester due to swelling. Praptowidodo *et al.* [206] prepared polyvinyl alcohol (PVA) of different crosslinking content to separate ethanol/water using pervaporation. They suggested that swelling of PVA lead to an increase in free volume which allowed more liquid to penetrate. They concluded that water flux increased and selectivity decreased, as a result of PVA swelling degree increased.

The crosslinking degree affects the polymer physical properties, such as polymer rigidity, and hence affects elastic resistance during the swelling process. Moreover, the crosslinking

degree affects free volume and polymer hydrophobicity/hydrophilicity, which in turn influences the sorption of components within the polymer. Simpson *et al.* [207] investigated the reactions between vinyl ($-\text{CH}=\text{CH}_2$) end groups on PDMS and SiH groups in a cross-linker. They concluded that addition of more cross-linker reduces membrane free volume and influences membrane performance. Qu *et al.* [208] studied PDMS crosslinking effects in gasoline pervaporation, and found that increasing crosslinking reduced the solvent-membrane interaction. They concluded that increasing membrane crosslinking restricted polymer swelling and decreased the sorption and diffusion rate leading to a decrease permeate flux. Similar results were obtained with PVA crosslinking by Yu *et al.* [209], who found that increasing PVA crosslinking density reduced permeate flux and increased selectivity. They concluded that isopropanol is difficult to permeate through a PVA structure due to its relatively large molecular size.

2.6.3 Quantification of membrane selectivity

Membrane selectivity arises from sorption selectivity and diffusion selectivity [86]. If there is no selectivity due to sorption there will be no selectivity due to diffusion, because there is no resulting gradient in chemical potential for separation to occur [49]. This section explores the potential to quantify the membrane sorption selectivity using:

1. Sorption coefficient
2. Flory-Huggins theory

2.6.4 Sorption coefficient

The starting point for the mathematical description of polymer swelling in mixtures is that, at equilibrium, the chemical potential of any species in the liquid equals the chemical potential of that species within the polymer. It is expressed as:

$$\mu_{ls}^{\wedge} = \mu_{lp}^{\wedge} \quad (2.12)$$

Where μ_{is}^{\wedge} is the chemical potential of component i in the solvent mixture, and μ_{ip}^{\wedge} is the chemical potential of component i in the polymer. The chemical potential of a substance can be further defined as [210]:

$$\mu_i^{\wedge} = \mu_i^0 + RT \ln \left(\frac{f_i^{\wedge}}{f_i^0} \right) \quad (2.13)$$

where μ_i^0 is the chemical potential of pure i at temperature T , f_i^{\wedge} is the fugacity of i in a mixture, and f_i^0 is the fugacity of pure i at saturation. By definition, the fugacity of i in a mixture is the product of the activity of species i (a_i), and the fugacity of pure i at the temperature and pressure of the mixture (f_i).

$$f_i^{\wedge} = a_i f_i \quad (2.14)$$

The activity of species i can be expressed as the product of the mole fraction (C_i) and the activity coefficient (γ_i).

$$f_i^{\wedge} = C_i \gamma_i f_i \quad (2.15)$$

The fugacity of a liquid at any pressure and temperature can be expressed relative to the fugacity at saturation, as shown in Equation 2.16 [211].

$$f_i = f_i^0 \exp \left[\frac{V}{RT} (P - P^0) \right] \quad (2.16)$$

where V is liquid molar volume, P is applied pressure, and P^0 is the saturation pressure at T .

$$f_i^{\wedge} = C_i \gamma_i f_i^0 \exp \left[\frac{V}{RT} (P - P^0) \right] \quad (2.17)$$

$$\text{From Equation 2.13: } \mu_i^{\wedge} = \mu_i^0 + RT \ln \frac{C_i \gamma_i f_i^0 \exp \left[\frac{V}{RT} (P - P^0) \right]}{f_i^0} \quad (2.18)$$

$$\mu_i^{\wedge} = \mu_i^0 + RT \ln (\gamma_i C_i) + V_l (P - P^0) \quad (2.19)$$

Equation 2.19 can be written for two cases; component i in a liquid mixture and component i in a swollen polymer.

$$\mu_{is}^{\wedge} = \mu_i^0 + RT \ln(\gamma_{is}C_{is}) + V_l(P - P^0) \quad (2.20)$$

$$\mu_{ip}^{\wedge} = \mu_i^0 + RT \ln(\gamma_{ip}C_{ip}) + V_{ip}(P - P^0) \quad (2.21)$$

Where γ_{ip} is the activity coefficient for component i in the polymer C_{ip} is the concentration of i in the polymer and V_{ip} is the molar volume of i within the swollen polymer matrix. Assuming that there is a negligible change in molar volume when in the liquid and swollen polymer then $V_l = V_{ip}$ [212]. Therefore, from Equation 2.12:

$$C_{ip} = \frac{\gamma_{is}}{\gamma_{ip}} C_{is} \quad (2.22)$$

Since the ratio of activity coefficients (γ_{ip}/γ_{is}) is the sorption coefficient, K_i [74], then equation 2.22 becomes

$$C_{ip} = K_i C_{is} \quad (2.23)$$

Rearranging equation 2.23 gives:

$$K_i = \frac{C_{ip}}{C_{is}} \quad (2.24)$$

Where C_{is} is equilibrium molar concentration of component i in the liquid mixture, and C_{ip} is final equilibrium molar concentration of i within the liquid in the polymer. Equation 2.24 is based on fundamental phase equilibrium, and the key assumption is that there is no change in the molar volume of species i between the liquid phase and the swollen polymer phase. The solvent concentration in the swollen polymer was used to calculate the sorption coefficient of solvent mixtures. The boundary conditions for sorption coefficient are:

$K_i > 1$, shows that membrane preferentially absorbs that solvent.

$K_i < 1$, shows that membrane does not selectivity absorbs the second component in the mixture.

$K_i = 1$ indicates no membrane selectivity.

2.6.5 Flory-Huggins theory

A theoretical approach developed by Paul Flory and Maurice Huggins [213] is based on a model that could be used to describe the non-ideal behaviour of polymeric solutions. They proposed that a low molecular-weight solvent and a high molecular-weight polymer are mixed by the movement of low molecular weight solvent in the polymer chain free volume, in the same way that solvent molecules move in solution [214]. The theory assumes that transport through polymers requires a free-volume, which is related to the space between polymeric chains; these volumes are available for mass transfer, where the absorbed molecules can diffuse [215-216].

$$\ln a_{is} = \ln \Phi_{is} + \left(1 - \frac{V_{is}}{V_{ip}}\right) \Phi_p + \chi_{sp} \Phi_p^2 \quad (2.25)$$

$$\ln a_{is} = \ln \Phi_{is} + \Phi_p + \chi_{sp} \Phi_p^2 \quad (2.26)$$

where a_{is} is solvent activity, Φ_{is} and Φ_p are volume fractions of solvent and polymer, V_{ip} is the polymer molar volume, V_{is} is the solvent molar volume, and χ_{sp} is known as the Flory-Huggins binary interaction parameter.

The dimensionless parameter χ_{sp} refers to the mixing energies, which take into account the energy of interdispersing polymer and solvent molecules. As affinity or interaction between polymer and the solvent increases, the amount of liquid inside the polymer increases and χ_{sp} decreases [217].

Equation 2.25 is the mathematical expression of the Flory-Huggins theory. The molar volume of the polymer (V_{ip}) is considered to be significantly larger than the solvent molar volume, and so their ratio is negligibly small; therefore, Equation 2.25 reduces to Equation 2.26. Equation 2.26 is one of the interpretations of the Flory-Huggins theory. This theory is

a good starting point to describe polymeric solutions, which allows equilibrium to be quantified using the Flory-Huggins binary interaction parameter, χ_{sp} . Flory Huggins is a realistic method to describe binary swelling (i.e. one polymer swelled by one solvent) and its validity for this binary mixture has been already established. The use of Flory-Huggins theory should be formally limited to non-crystalline, non-crosslinked polymers [218]. Despite these limitations, the Flory-Huggins equation has already been shown to give an excellent description of solvent sorption in crosslinked polymer [219]. The interaction parameter is used to analyse polymer/solvent compatibility. Numerically, if the interaction parameter value < 0.5 for a polymer and solvent, therefore polymer and solvent are completely miscible over the entire composition range. Bhanushali *et al.* [179] estimated the type of interactions between the polymer and the solvent based on the qualitative value of interaction parameter. For example, when values < 0.5 , the interactions were very large, and the polymer and solvent were compatible, often leading to the polymer dissolving in the solvent. However, for values of interaction parameters > 1 , which were considered large, the interactions were small between the chosen polymer and solvent. The Flory Huggins parameter for binary system could be used to predict the separation by the membrane in a ternary system. For example, a mixture of A and B, where A is present in a very low amount and is to be separated, the interaction parameter of A must be lower compared to the other component B for a particular membrane polymer. This was observed by Mandal *et al.* [193], who used the interaction parameter for binary system to predict separation in a ternary system. In a mixture of A and B, the interaction parameter ratio between permeate components, A and B, through the membrane, is a measure of preferential sorption for A and B in the membrane (M). For example, if

component A is desired to permeate and component B is to be rejected, then membrane material should be selected to minimise the ratio χ_{AM}/χ_{BM} .

2.6.5.1 Application of Flory-Huggins theory to ternary mixtures

The Flory-Huggins model has been used to quantify the behaviour of ternary mixtures (i.e. one polymer, p , and two solvents, s_1 and s_2). Equation 2.25 can be readily extended to ternary mixtures, leading to the following non-linear equation system [220]:

$$\ln a_{s1} = \ln \Phi_{s1} + (1 - \Phi_{s1}) - \left(\frac{V_{s1}}{V_{s2}}\right) \Phi_{s2} - \left(\frac{V_{s1}}{V_p}\right) \Phi_p + \left((\chi_{s1s2} \Phi_{s2} + \chi_{s1p} \Phi_p)(\Phi_{s2} + \Phi_p)\right) - \chi_{s2p} \cdot \left(\frac{V_{s1}}{V_{s2}}\right) \cdot \Phi_{s2} \cdot \Phi_p \quad (2.27)$$

$$\ln a_{s2} = \ln \Phi_{s2} + (1 - \Phi_{s2}) - \left(\frac{V_{s2}}{V_{s1}}\right) \Phi_{s1} - \left(\frac{V_{s2}}{V_p}\right) \Phi_p + \left((\chi_{s1s2} \Phi_{s1} \left(\frac{V_{s2}}{V_{s1}}\right) + \chi_{s2p} \Phi_p)(\Phi_{s1} + \Phi_p)\right) - \chi_{s1p} \left(\frac{V_{s2}}{V_{s1}}\right) \Phi_{s1} \Phi_p \quad (2.28)$$

$$\Phi_{s1} + \Phi_{s2} + \Phi_p = 1 \quad (2.29)$$

2.6.5.2 Application of Flory-Huggins to solvent/solvent mixtures

Equation 2.25 can be extended to solvent/solvent interaction parameters [220].

$$\ln a_{s1} = \ln \Phi_{s1} + \left(1 - \frac{V_{s1}}{V_{s2}}\right) \Phi_{s2} + \chi_{s1s2} \Phi_{s2}^2 \quad (2.30)$$

$$\ln a_{s2} = \ln \Phi_{s2} + \left(1 - \frac{V_{s2}}{V_{s1}}\right) \Phi_{s1} + \chi_{s1s2} \frac{V_{s2}}{V_{s1}} \Phi_{s1}^2 \quad (2.31)$$

The determination of liquid-liquid interaction parameters (χ_{s1s2}) can be performed by calculating the solvent activity using Vapour Liquid Equilibrium (VLE) data, as χ_{s1s2} is a function of solvent volume fraction only. The average value for χ_{s1s2} could be applied to the Flory-Huggins equation for ternary system.

2.6.5.3 Previous studies of organic/water systems using the Flory-Huggins model

Few studies have been concerned with the evaluation of Flory-Huggins in ternary mixtures, despite the importance of this type of mixture for many applications, Han *et al.* [221] analysed swelling based on the Flory Huggins model to propose a permeation model for isopropanol/water/PVA systems. They concluded that the predicted solvent volume fraction in membrane and permeate flux are in good agreement with the experimental data.

Nguyen *et al.* [205] reported that the Flory Huggins model was not valid for water sorption in PDMS, due to the clustering of absorbed molecules in the swollen polymer. Flory Huggins can predict sorption of many organic solvents, whilst ethanol sorption requires a more sophisticated approach in order to fit its sorption behaviour to isotherms. Schaetzel *et al.* [222] suggested that Flory Huggins model quantitatively predicts ethyl acetate sorption through a PDMS membrane, as the system ethyl acetate/PDMS can be qualified as an ideal system in diffusion, however the prediction is less satisfactory for water/ethanol/PVA membrane due to polar effects. Pitol-Filho *et al.* [223] used the swelling experiments in ternary system for methanol, ethanol, isopropanol, and 1-octanol in water, and found that these systems did not fit the solvent activity predicted by Flory Huggins equilibrium, due to the very polar character of such compounds. Vergara *et al.* [224] confirmed that other theories are needed to predict systems involving polar and hydrogen-bonding forces.

The Flory Huggins theory can be used to assess the sorption of various components from swelling equilibrium data. However, Flory Huggins model is not always valid in the description of the sorption of solvents mixture in polymers. The systems involving polar and hydrogen-bonding effects could not predicted by the Flory Huggins. The unpredictable sorption values due to polar solvents could be attributed to the interaction between the incoming solvent molecule and an already absorbed solvent molecule.

Some literature suggested a clustering model to describe the behaviour of alcohols and ketones. Clustering behaviour is due to the presence of hydrogen bonding, which inhibits the absorption of molecules containing -OH groups. Wong *et al.* [225] investigated PVA/water/methanol and found that Flory Huggins model is not always valid in the description of the sorption of solvents mixture in polymers. They suggested that the non-validity of the Flory Huggins equation could be attributed to the clustering of absorbed

molecules. Favre *et al.* [220, 226] observed excellent agreement of the Flory-Huggins model for PDMS and hydrocarbons. However poor swelling solvents (alcohols, methyl ethyl ketone) in crosslinked silicone membranes were inadequately described by Flory-Huggins theory. They observed that failure occurred when the polymer-solvent interaction parameter value exceeds 0.8, which reflects the limit above which penetrant-penetrant interactions were stronger than those of penetrant-polymer. Their hypothesis was confirmed by an analysis based on a clustering criterion developed by Zimm and Lundberg [227] who suggested that cluster formation occur at high solvent activity.

2.6.5.4 Comparison between Flory- Huggins model and actual activity

The method used in this thesis is to investigate the applicability the Flory- Huggins model by comparing it with the actual activity from vapour-liquid equilibrium. A comparison between actual solvent activities and experimental solvent activity will enable the validity of Flory-Huggins theory to be evaluated. The actual solvent activities can be calculated by one of the classical equations used for vapour-liquid equilibrium (i.e van Laar) [228].

The experimental solvent activity calculations demand the three molar volumes, V_{s1} , V_{s2} , and V_p , and three interaction parameters, (χ_{s1p}) , (χ_{s2p}) and (χ_{s1s2}) , to be known for solvents S_1 and S_2 , and polymer respectively. Since molar volume of the polymer (V_p) is most often considered to largely overwhelm the solvent molar volume, then solvent/polymer molar volume ratio (V_s/V_p) can be approximated as equal to zero [229]. The solvent activity in the ternary system can be calculated using Equations 2.27 and 2.28, based on the following procedure:

- (i) Interaction parameters (for χ_{slp} and χ_{s2p}) are calculated from polymer swelling in pure solvent, and solvent1/solvent2 interaction parameter, χ_{s1s2} , from VLE.

CHAPTER TWO LITERATURE REVIEW

(ii) The interaction parameters, molar volumes (V) and experimental swelling data can be used to calculate activity by Equations 2.27 and 2.28.

(iii) At equilibrium, solvent activities in the liquid and in the swollen polymer are identical. The actual activity coefficient was calculated by the Van Laar method for comparison with that calculated by Flory-Huggins model. In compliance with the recommendations in thermodynamic Tables [228], Van Laar is a well recognized activity coefficient method for liquid mixtures and is shown in Equation 2.32 and 2.33.

$$\ln \gamma_1 = A_{12} \left(\frac{A_{21}C_2}{A_{12}C_1 + A_{21}C_2} \right)^2 \quad (2.32)$$

$$\ln \gamma_2 = A_{21} \left(\frac{A_{12}C_1}{A_{12}C_1 + A_{21}C_2} \right)^2 \quad (2.33)$$

$$a_i = \gamma_i C_i \quad (2.34)$$

Where A_{12} and A_{21} are the activity coefficient parameters between solvent₁ and solvent₂, and C_1 and C_2 are molar concentrations of the two solvents respectively. The actual activity coefficient parameters A_{12} and A_{21} are shown in Table 2.2.

Table 2.2 Activity coefficient parameters of solvent mixtures [230].

System	A_{12}	A_{21}
Ethanol/n-hexane	1.93820	2.62819
Ethanol/n-heptane	2.26942	2.29424
Ethanol/water	1.69734	0.98127
Isopropanol/water	2.9635	1.18842

Chapter 3 EXPERIMENTAL

3.1 Introduction

This chapter describes the materials, equipment and protocols adopted for each experiment in this study. It is divided into five sections.

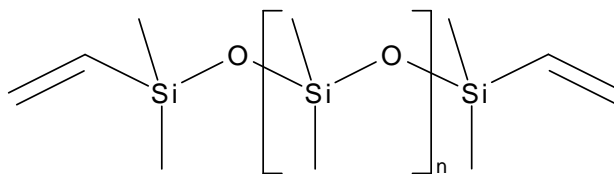
The first two sections explain the preparation, washing and drying, as well as the characteristics of the PDMS and PVA polymers used in this study and their crosslinking methods.

The third section describes polymer swelling in pure solvents, followed by the measurements undertaken during the swelling process and subsequent calculations and analysis. The final section describes the novel apparatus used for swelling measurements under different pressures, and details the apparatus, procedure and measurement methods.

3.2 Preparation of PDMS

3.2.1 Materials

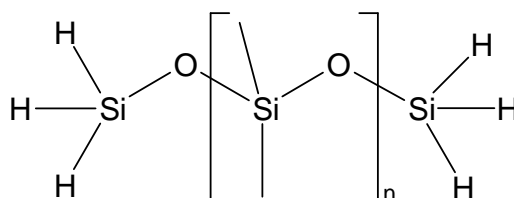
PDMS was manufactured by a crosslinking reaction between pre-polymer component (RTV615A) and crosslinker (RTV615B). These two liquid compounds were provided by TECHSIL Ltd [231]. RTV615A consists mainly of long PDMS oligomers capped by vinyl groups as shown in Figure 3-1.



RTV615A

Figure 3-1 Structure of RTV615A showing the PDMS reactive vinyl end groups

RTV615B consists of shorter PDMS oligomers with silicon hydride groups, as shown in Figure 3-2.



RTV615B

Figure 3-2 Structure of RTV615B showing the PDMS SiH₃ end functional groups

3.2.2 Crosslinking reaction

The reaction depends on the amount of both RTV615A and RTV615B in the reaction mixture. By varying the ratio of RTV615A and RTV615B, the final PDMS will have different characteristics. Figure 3-3 shows the crosslinking reaction (hydrosilylation), which depends on the ability of the hydrosilane bond of the cross-linker (Si-H) to add a cross carbon-carbon double bond that belongs to the pre-polymer, forming Si-CH₂-CH₂-Si linkages [232]. The multiple reaction sites on both the pre-polymer and crosslinker oligomers allow for three-dimensional crosslinking [233]. One advantage of this type of addition reaction is that no condensation products are generated. If the ratio of crosslinker to pre-polymer is increased, a harder, more cross-linked PDMS results.

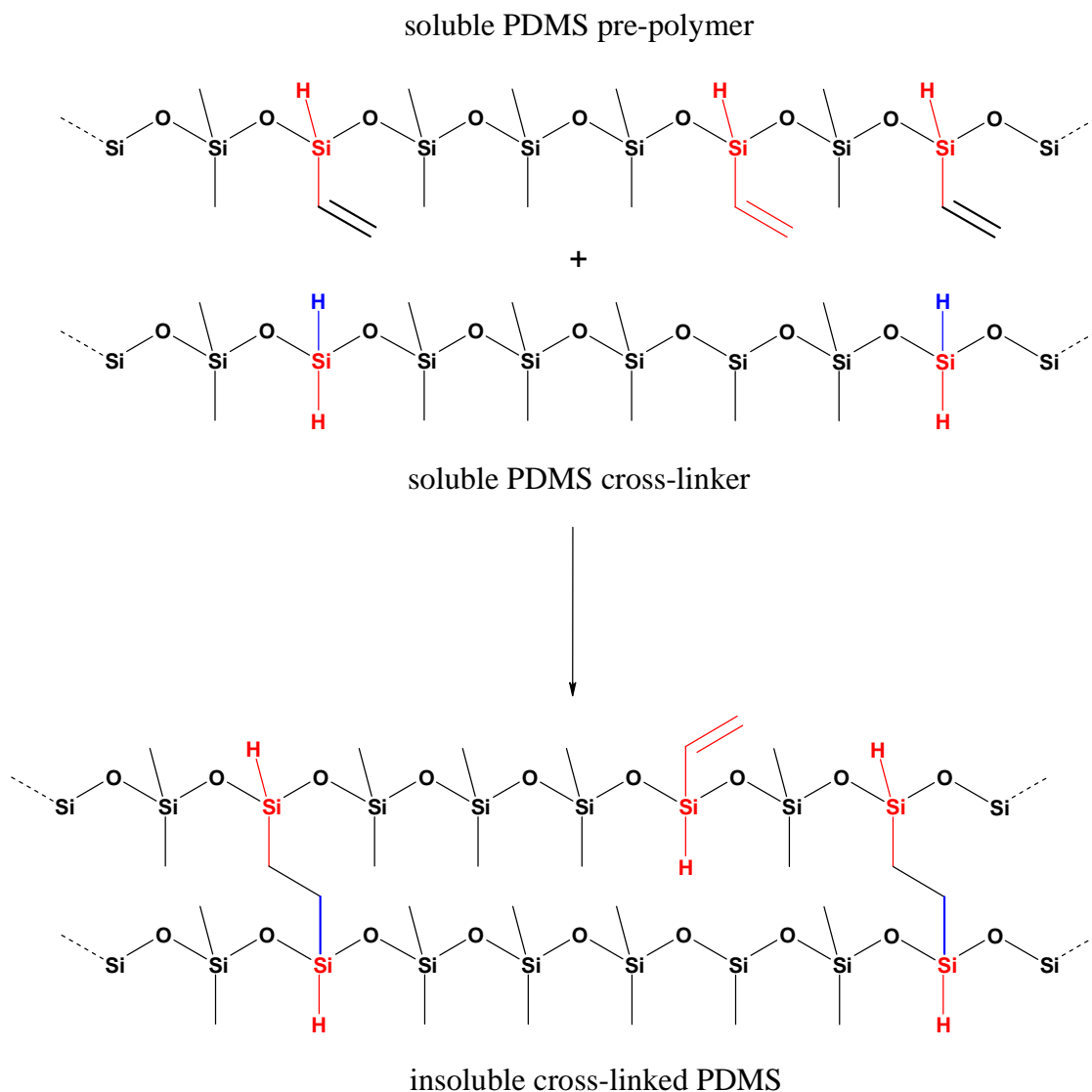


Figure 3-3 Schematic illustrating crosslinking reaction of PDMS. Reaction of the Si-H with C=C bond to form the new Si-C bond (—).

The pre-polymer contains vinyl groups and the cross-linker contains the SiH functional groups. The red and blue coloured lines in Figure 3-3 shows the linkage, crosslinking the polymer chains and connecting them together to form one network. This connection could occur at any point along the polymer chain, so the structure in Figure 3-3 does not necessarily represent that which would be obtained for every crosslinking reaction.

3.2.3 Different crosslinking contents

The PDMS polymer was prepared by mixing a weight of RTV 615A with RTV 615B at different ratios, corresponding to crosslinking degrees of 5, 10, 15, 20, and 25 wt%. All polymer samples were allowed to complete the reaction at 60 °C for 6 hours. The degree of crosslinking was calculated using the following equation:

$$\text{crosslinking content} = \frac{\text{weight of RTV615B}}{(\text{weight of RTV615B} + \text{weight of RTV615A})} \% \quad (3.1)$$

The manufacture of a dense block of PDMS required a mould container, in which the reaction could take place. A glass tube of 20 mm diameter and 80 mm length was used. All glassware was rinsed with de-ionised water and dried at 70 °C overnight. The samples were weighed using a highly sensitive electronic balance (Mettler Toledo ML204) with an accuracy of 0.0001 g. Clean and dry glass beakers were weighed, and then RTV615A was weighed in the beaker. The required weight of RTV615B was poured over the RTV615A. The weight of the beaker was recorded and then taken off the balance. RTV615A was mixed for 5 minutes with RTV615B components using clean glass tools. Mixing of RTV615A and RTV615B was allowed in a container 4-5 times larger than the volume of the RTV615 compounds. The sides and bottom of the container were carefully scraped to achieve a homogeneous mixture. Excessive mixing speeds were avoided, as this could entrap large amounts of air or cause overheating of the mixture.

The mixed PDMS was poured into the glass mould. The glass containing the polymer was put in an oven, and the final mixture was allowed to cure at 60°C for 6 hours. After curing the glass mould was broken and removed. The crosslinked PDMS remained in the shape of the mould. The polymer was cleaned of attached glass pieces before being weighed. When the glass was broken, a visual inspection of the polymer was performed to avoid using material with excessive cracks or fissures present. In this way, a consistent sample of final

polymer in the shape of the mould was obtained. The PDMS samples were prepared in dense blocks to allow measurement of swelling equilibrium. The blocks were then cut to size, 15 mm (diameter) and 10 mm (length), in order to measure the swelling abilities in a solvent or mixture of solvents. This procedure was repeated to prepare different samples with different crosslinking degrees.

3.2.4 Washing

For the polymer to give consistent and repeatable swelling results it is necessary to extract the soluble component from crosslinked PDMS, i.e. un-reacted base component. This was achieved by washing the polymer in toluene and allowing it to swell; with the washing process conducted over three cycles. The polymer was weighed before starting the washing cycles, and the mass loss was monitored to ensure that all unreacted base components were removed by the end of the final cycle. The drying process was carried out by removing the PDMS from the liquid and allowing it to dry in air under atmospheric conditions. Figure 3-4 shows an example of the washing cycles for PDMS (crosslinking degree 5%). The swelling degree at equilibrium (SD %) is expressed as a percentage according to Equation 3.2.

$$SD\% = \left(\frac{m_{fp} - m_{ip}}{m_{ip}} \right) \times 100 \quad (3.2)$$

Where m_{fp} is the final swollen weight, and m_{ip} is the initial weight of dry polymer

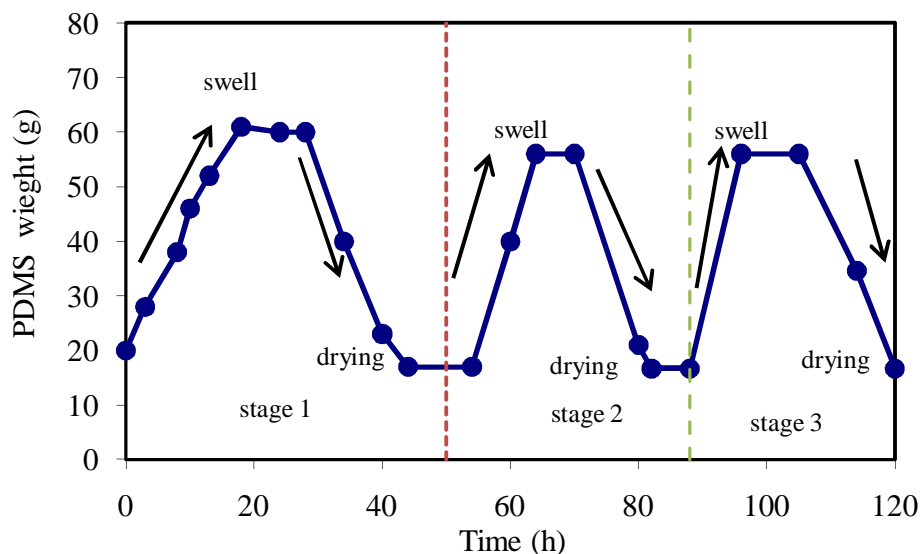


Figure 3-4 Sample swelling data for PDMS washed for 3 cycles in toluene

In the first stage, PDMS was immersed in toluene and allowed to swell from its starting mass of 20 g. The mass increase was monitored over time, until it reached a maximum at 61 g. Once the initial maximum was attained the PDMS was left in the liquid for 10 hours. The drying process was carried out by removing the PDMS from the liquid and allowing it to dry in air under atmospheric conditions. The final weight of PDMS was 17.0 g, which indicates a reduction of 3.0 g from the initial mass, and corresponds to un-reacted base component extracted from the PDMS and dissolved in toluene.

In the second stage, the mass of swollen polymer reached a maximum of 56 g, which when dried reduced to 16.6 g, losing a further 0.4 g of un-reacted polymer. In the third stage, PDMS swelled to 56 g which is the same as in the second stage. After the final drying process, the mass was again 16.6 g, i.e. the same dry mass as in the second cycle. This indicates that no further un-reacted polymer was present in PDMS after 3 cycles of washing with toluene.

In this case swelling/drying gives a final PDMS weight of 16.6 g, the total dissolved unreacted polymer was 3.4g. The unreacted component is RTV615A, as it is assumed that all the cross linker RTV615B reacts completely with RTV615A. Therefore, the weight loss observed was a result of any excess or unreacted RTV615A [234].

The final crosslinking content can be calculated as mass of RTV615B divided by the final PDMS mass; 6% in this case. It is important that the experimental results take into account the loss of RTV615A during the washing cycles. For each sample of polymer used, the actual crosslinking ratio was calculated based on the mass of RTV615A present in the polymer after the washing cycles, rather than the mass used to make the polymer during the curing process. Table 3.1 shows PDMS final crosslinking degree after the 3 washing cycles. Similarly, Nguyen *et al.* [205] extracted unreacted species from their PDMS samples by repeated washing with acetone after the crosslinking reaction. This work used toluene as it has a high affinity for dissolving unreacted RTV615A.

This study indicates that swelling takes 18 hours to reach equilibrium. However Tarleton *et al.* [183] reported that sixty seconds were sufficient for a PDMS membrane of 10 μm thickness to reach equilibrium. There is clearly a difference between the results obtained in this study and those of Tarleton *et al.* [183]. It is thought that this difference may be attributed to one or all of the following:

1. In this study a block of 10 mm thickness polymer was used, a factor of 10^3 different to that used in the previous study. If the same swelling rate occurred in both samples it would expect that swelling time reported by Tarleton *et al.* [183] could be multiplied by 10^3 , which results in a swelling time of 17 hours. This is consistent with the observations reported in this work.

2. The difference in crosslinking methods employed in both studies. The crosslinking method used in this study is a thermal crosslinking method (as explained detailed in Section 3.2.3), whereas Tarleton *et al.* [183] used membranes manufactured using a radiation crosslinking technique. The nature and properties of the polymers used in each case could be very different based on both the degree of crosslinking and the crosslinking method.

Table 3.1. PDMS final crosslinking degree after 3 washing cycles in toluene

Initial crosslinking (%)	RTV615A initial mass (g)	RTV615B initial mass (g)	RTV615A lost in washing (g)	Final crosslinking (%)
5	19	1	3.40	6.0
10	18	2	2.04	10.9
15	17	3	1.06	15.7
20	16	4	0.42	20.4
25	15	5	0.05	25.0

The results in Table 3.1 show a decrease in the amount of RTV615A removed during washing with increasing RTV615B. The data demonstrate how the final crosslinking content increases as the ratio of RTV615A to RTV615B decreases.

3.2.5 Validity of swelling measurement technique

For assessment of the validity of the swelling measurement technique, the effect of drying on the swollen polymer was investigated. A piece of 16.6 g PDMS was allowed to swell in toluene, the swollen polymer was dried on the balance, and the weight of swollen PDMS was recorded over 15 minutes. Figure 3-5 shows the effect of time on the mass of swollen PDMS during drying.

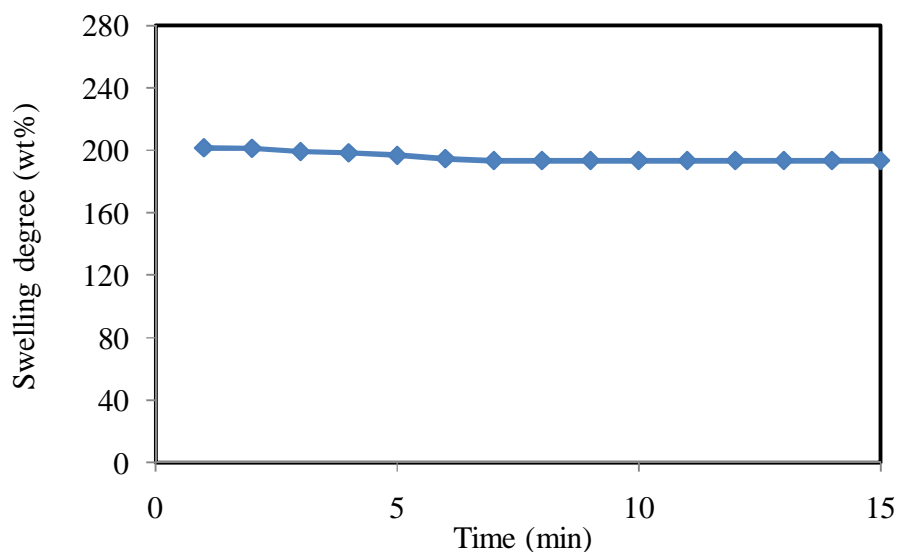


Figure 3-5 Drying of swollen PDMS over time

Figure 3-5 shows the drying of PDMS sample over 15 minutes. After swelling was achieved, the polymer was removed from the liquid and weighed at room temperature. Excess solvent on the polymer surface was dabbed away with a tissue. Figure 3.5 indicates that minimal desorption of liquid will occur from the swollen polymer during this process. To confirm the validity of the technique, a reference piece of swollen PDMS was not dabbed with a tissue and weighed directly. The difference in weight between the reference and the dabbed polymer was 0.015 g, compared to the initial weight of 16.6 g. The results indicate that loss of absorbed solvent due to dabbing with the tissue was negligible, and in the most extreme case the maximum error is 0.03% of the swollen polymer weight.

The polymer was allowed to dry on the balance, at the first minute the polymer swelling degree was 201 wt%, then polymer was left on the balance for 15 minutes, and the weight recorded. The liquid evaporates from the swollen polymer, hence the polymer weight decreases. After 15 minutes polymer weight was recorded and swelling degree was

calculated (193 wt%); thus the evaporation rate for the first 15 minutes was 0.12 g/ minute. If the drying line was extended, polymer swelling degree at time 0 will be 201.8 wt%. Compared to polymer initial swelling degree 201 wt%, the difference indicates that when the swelling measurement was performed within one minute of removing polymer from liquid, then the change in weight due to drying will be no more than 0.8 wt% of the final swelling degree. Of note is that the swelling degree at the end of the drying stage is 0 wt%, when compared to polymer initial swelling degree of 212 wt%, the difference indicates that the change in weight in the first minutes is negligible.

The results show if the measurement is performed within one minute of the sample taken out of liquid, then recorded polymer swelling degree will be within 0.8 wt% of the actual value. In conclusion the evaporation of surface liquid does not impact on the accuracy of the results obtained using this method.

3.3 Preparation of crosslinked polyvinyl alcohol PVA

PVA has a poor stability in aqueous solutions, so crosslinking was used to create a stable PVA polymer. “PVAc” denote the starting pre-polymer material and “PVA” refer to the final crosslinked polymer.

3.3.1 Materials

The polymer was manufactured using poly(vinyl alcohol) powder, PVAc with an average molecular weight of 89,000-98,000. Glutaraldehyde (GA) is a solution of 25 wt % concentration in water, and hydrochloric acid were both supplied by Sigma- Aldrich.

3.3.2 PVA crosslinking reaction

Poly(vinyl alcohol) is a semi-crystalline polymer that changes its structure after the crosslinking reaction. PVA crosslinked structure was created by reaction between hydroxyl groups in PVAc and aldehyde groups in dialdehydes, such as GA, in the presence of a hydrochloric acid catalyst. The crosslinking reaction (acetylation) between PVAc, which contains hydroxyl groups with the aldehyde groups in GA depends on the crosslinker loading during the crosslinking reaction. The acetylation reaction produces three structures [185] as shown in Figure 3-6, 3-7 and 3-8.

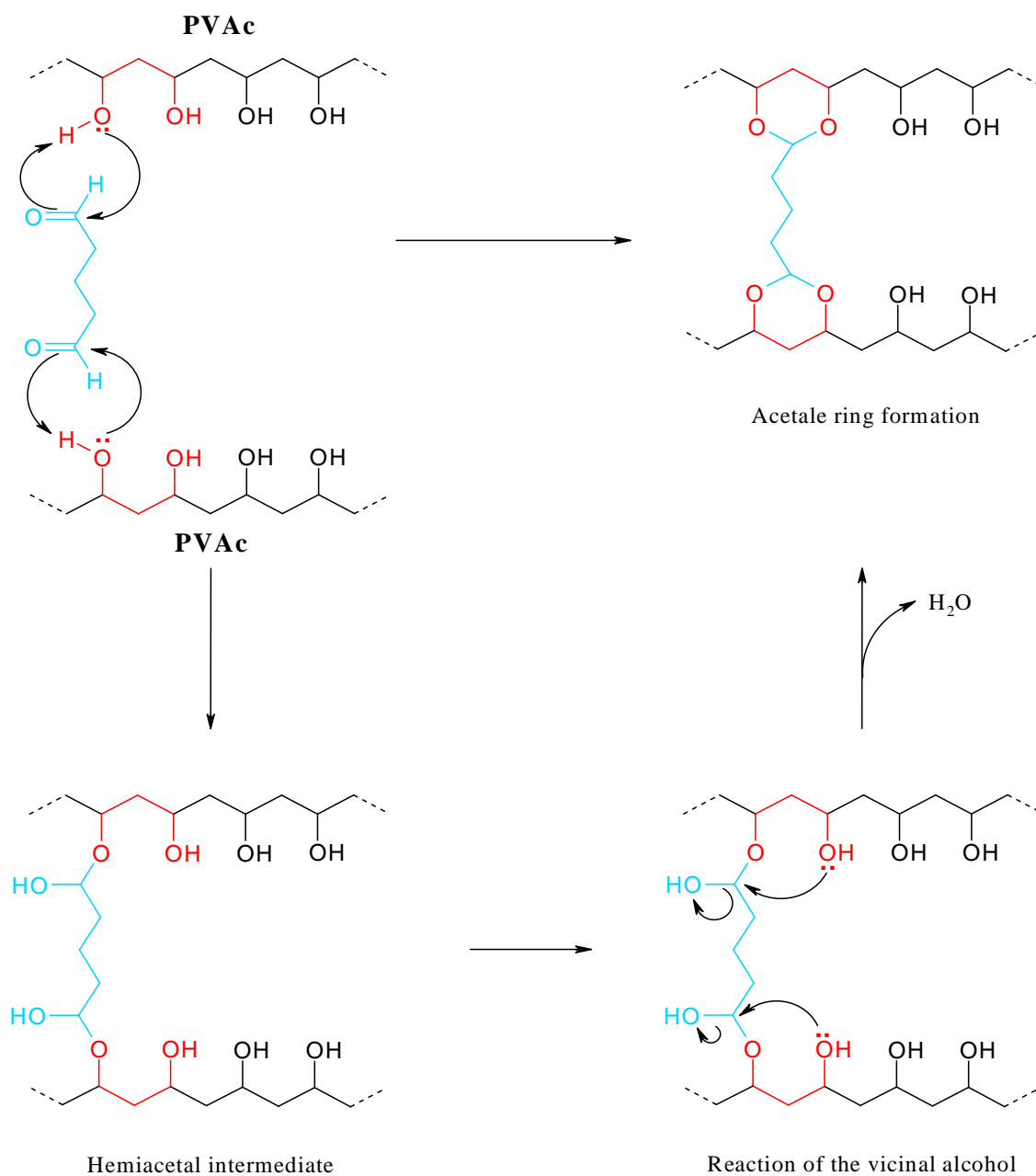


Figure 3-6 Crosslinking reaction between PVAc and GA and the formation of structure 1 (acetal ring groups)

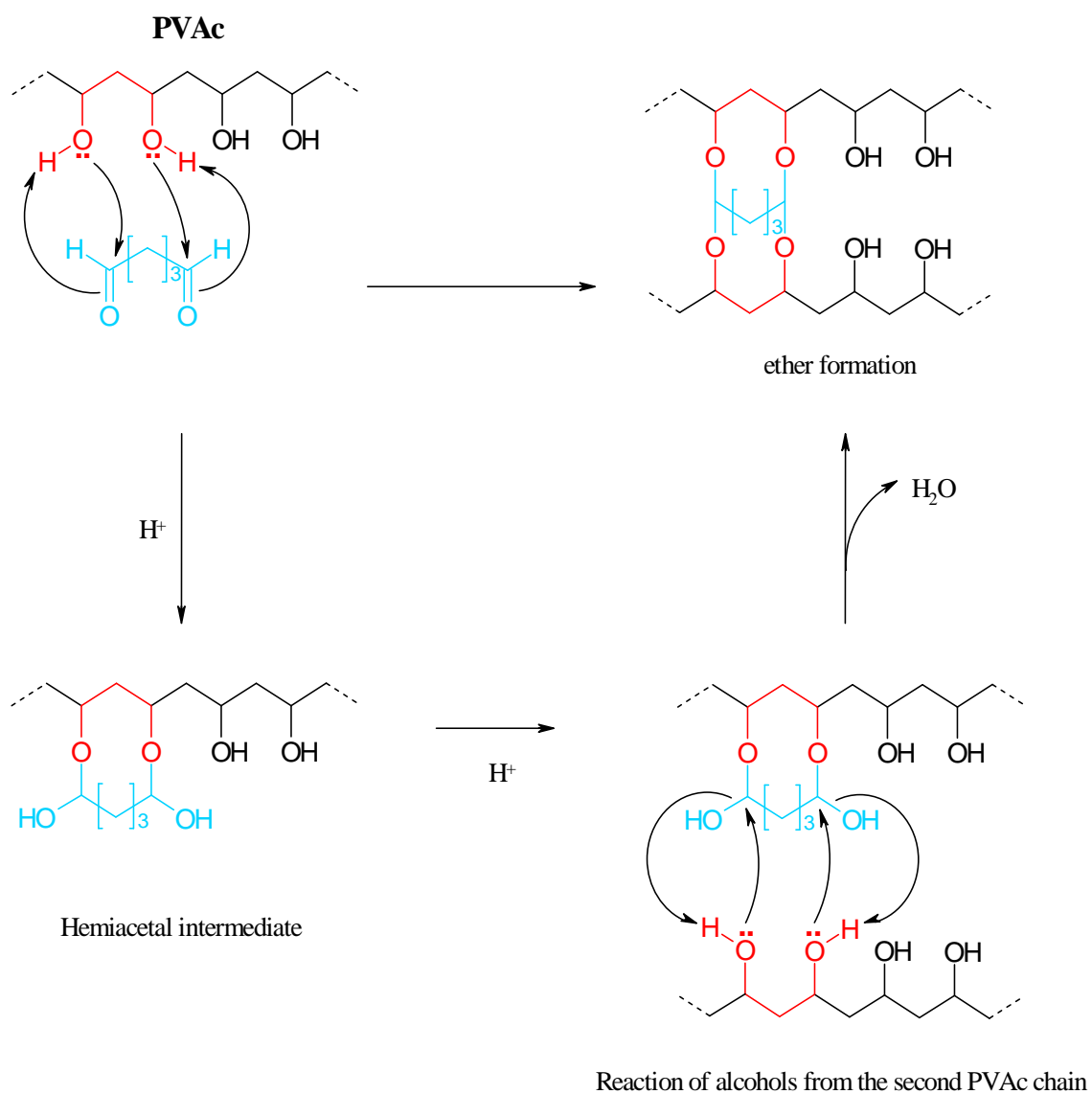


Figure 3-7 Crosslinking reaction between PVAc and GA and the formation of structure 2 (ether linkages)

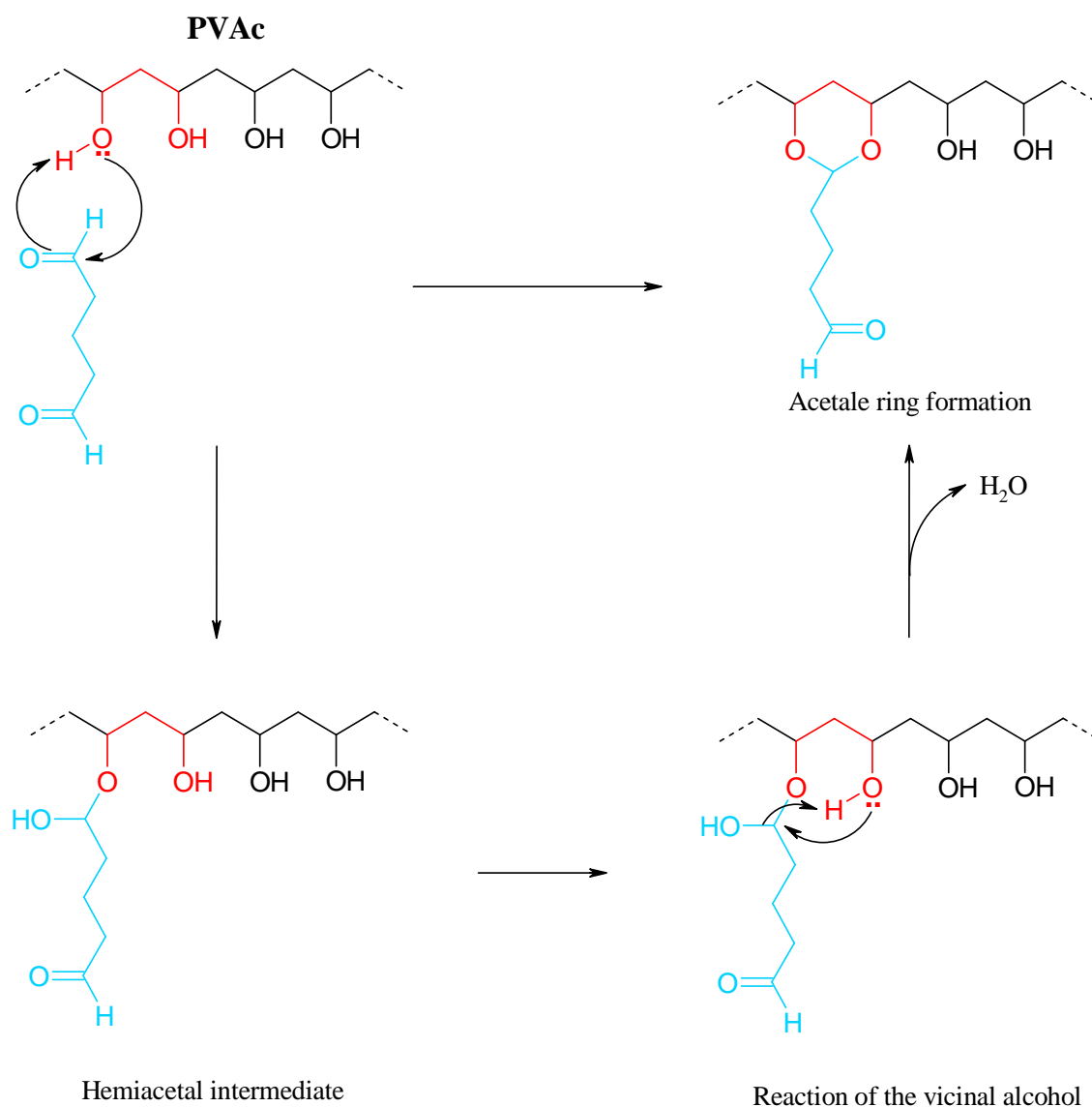


Figure 3-8 Crosslinking reaction between PVAc and GA and the formation of structure 3 (aldehyde linkage formation)

The hydroxyl groups in the poly(vinyl alcohol) react with the aldehyde groups during the crosslinking reaction. Typical products from the reaction are acetal groups or ether linkages in the polymer network or mono aldehyde group.

Structure 1: The reaction occurred between the hydroxyl groups from the same polymer chain with one aldehyde leading to the formation of an acetal ring group. Structure 2: The reaction occurred between the hydroxyl groups from two polymer chains with one aldehyde group leading to the formation of an ether linkage. Structure 3: The reaction occurred between the hydroxyl groups from the same polymer branch with one aldehyde leading to the formation of an acetal ring group, however the other aldehyde group does not react (in case of excess GA in the reaction solution).

When the PVAc concentration is higher than GA in the reaction medium the formation of structure 1 and structure 2 can occur. However, with increasing GA in the reaction medium, structure 3 can occur. PVAc contain a large number of –OH groups, not all of which can react with the aldehyde during the limited crosslinking time, leading to the formation of structure 3 by mono-functional reactions [185].

3.3.3 PVA different crosslinking content

The crosslinking content was calculated as the weight of GA in the reaction solution as a proportion of the combined weight of PVAc and GA. PVA polymers were previously prepared in a form of a thin membrane film [105-112]. To the knowledge of the author the investigation of swelling of a block of dense PVA has never been performed before.

For the purpose of studying the effect of crosslinker loading on crosslinked PVA swelling degree, the crosslinked polymers were prepared with 5, 10, 15, 20, and 25 wt% GA.

$$\text{crosslinking ratio} = \frac{\text{weight of GA}}{(\text{weight of GA} + \text{weight of PVAc})} \% \quad (3.3)$$

Crosslinked PVA was prepared by dissolving 19g of PVAc powder in 50ml deionised water. The solution was heated and stirred at 60 °C until complete dissolution was achieved. A glass cylinder of 20 mm diameter and 80 mm length was used as a mould.

GA was diluted to 2.5 wt% before use as crosslinker [105, 119]. When the GA solution content was less than 2.5 wt% in the reaction solution, insufficient crosslinking occurred due to a lack of crosslinking agent; hence, the resulting polymer dissolved partially or completely in water. Stable polymers could be prepared with GA solution content at or above 2.5 wt%. The crosslinker solution was prepared by mixing 1g of GA 2.5 wt% and 1 g of 36 wt% hydrochloric acid solution. The crosslinker solution was added to the PVAc solution, and the mixture left to crosslink for 4 hours at 40°C [235]. After curing, the glass mould was broken, and any attached glass pieces removed from the polymer. The crosslinked PVA remained in the shape of the mould. This procedure was repeated to prepare different samples using different ratios of the PVAc and crosslinker. Crosslinked PVA polymer samples were prepared in blocks of 15 mm and 60 mm length. The PVA samples sizes are different from PDMS sample sizes which is due to the swelling degree of PDMS is higher than that of PVA.

3.3.4 PVA washing

The excess addition of crosslinker or pre-polymer will lead to a network with different chemical and mechanical properties. The crosslinked polymer was washed to eliminate residual unreacted component, the washing process followed a method established in the literature [185, 209]. Crosslinked PVA was washed over three cycles in water to eliminate unreacted GA from the final polymer, as the addition of extra crosslinker will be removed from the final crosslinked polymer [95, 209, 236].

The PVA polymer was weighed before starting the washing cycles. The polymer was washed with water and allowed to swell, with weight recorded over time until equilibrium was reached. It was then removed from the water and allowed to dry with the weight recorded over time. The washing was repeated in 3 cycles with water, and mass loss

monitored to ensure that all un-reacted component were removed by the end of the final cycle. Figure 3-9 shows an example for PVA with 25% crosslinker content.

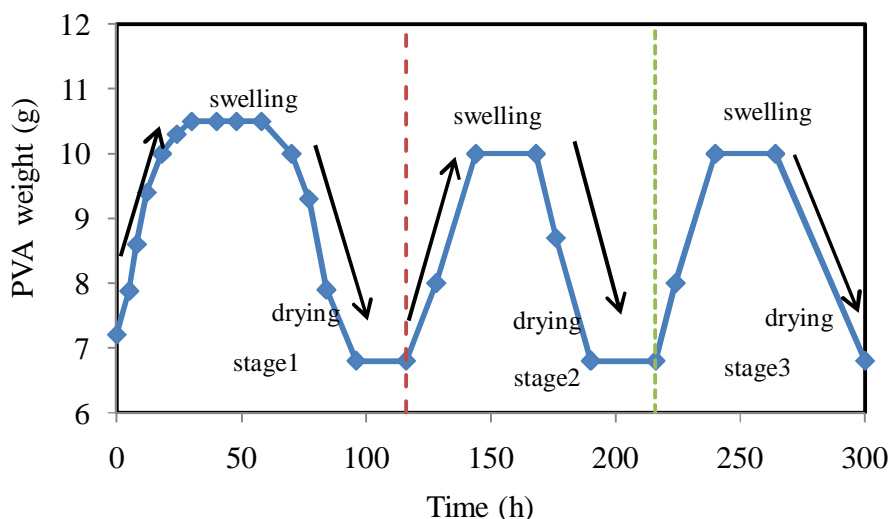


Figure 3-9 Swelling of crosslinked PVA in 3 cycles over three time intervals

In the first stage, crosslinked PVA was immersed in water and allowed to swell from its starting mass of 7.2 g. The mass increase was recorded at different time intervals, until it reached a maximum of 10.5 g. Once the initial maximum was attained the crosslinked PVA was left in the liquid for 20 hours. The drying process was carried out by removing the crosslinked PVA from the liquid, and allowed to dry in air under atmospheric conditions. The final weight of crosslinked PVA was 6.8 g. This indicates that 0.5 g unreacted crosslinker was extracted from the crosslinked PVA, and dissolved in water. In the second stage, the mass of swollen polymer reached a maximum of 10 g, then dried to 6.8 g. In the third and final stage, crosslinked PVA swelled to 10 g, which reduced to 6.8 g when dry. After this final drying process it can be seen that the mass was the same as after the second cycle, which indicates that 0.5 g un-reacted GA was extracted from the initial polymer. No further unreacted component were presented in crosslinked PVA after the 3

cycles of washing (and swelling) in water. Compared to Figure 3-4, the results indicate that the swelling degree of PVA is lower than that of PDMS.

Table 3.2. Final PVA crosslinking content after 3 washing cycles in water.

Initial crosslinking (wt%)	PVAc (g)	GA(g)	Lost in washing(g)	Final crosslinking (wt%)
5	19	1	0.00	5.0
10	18	2	0.04	9.8
15	17	3	0.16	14.3
20	16	4	0.40	18.4
25	15	5	0.50	23.0

The PVA washing process is different from PDMS washing, as washing PVA removes extra crosslinker from the final crosslinked [95, 209, 236]. However, washing PDMS removes excess pre-polymer from the final polymer. As was the case for PDMS, it was important to ensure that the experimental results take into account the loss of GA from polymer during the washing cycles. For each sample of polymer, the actual crosslinking ratio was calculated based on the mass of GA and PVAc present in the polymer after the washing cycles, rather than the mass used to manufacture the polymer during the curing process. The unreacted component extracted during washing increases with increasing GA weight. For example, at the ratio of GA/PVAc of 5/20, the amount lost by washing is 0.5g. However, for GA/PVAc at ratio 1/19, the mass of extractable component was negligible.

3.3.5 Validity of swelling measurement technique

After polymer swelling was performed, the polymer was removed from the liquid and the weight was recorded. The validity of the swelling measurement technique was investigated to assess the impact of removing the sample from liquid on the accuracy of results. Figure 3-10 shows the effect of time on polymer sample drying.

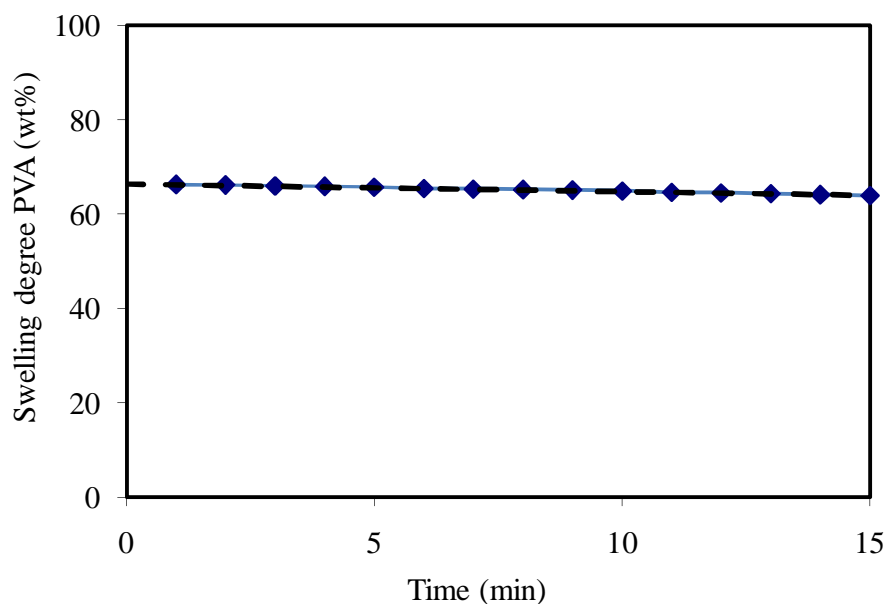


Figure 3-10 Drying of crosslinked PVA from water over time

The results show the weight of crosslinked PVA over 15 minutes during the drying process. After the swelling process was completed, the polymer was removed from the liquid, excess solvent dabbed away with a tissue (as explained in Section 3.2.5), and weighed at room temperature. The polymer swelling degree was 65.8 wt% in the first minute, then the polymer was left on the balance for 15 minutes and the weight recorded over time. The drying rate for the first 15 minutes was 0.06 g/ minute. If the drying trend is extended, polymer swelling degree at time 0 will be 65.82 wt%. Compared to their initial swelling degree (65.8 wt%), the change in weight due drying will be no more than 0.02 %.

3.4 Swelling in pure solvents

3.4.1 Materials

The solvents studied were ethanol (analytical reagent grade), isopropanol (analytical reagent grade). In order to study the effect of polarity on polymer swelling a wide range of polar solvents were studied such as methanol (reagent grade), n-butanol (analytical reagent grade), iso-butanol (analytical reagent grade), toluene (HPLC grade), xylene (HPLC grade), heptane (HPLC grade), and hexane (HPLC grade) which were obtained from Fisher Scientific. Demineralised water was sourced from a milpore unit (Milli-Q PLUS 185), and had a conductivity of $4 \mu\text{S.m}^{-1}$.

3.4.2 Polymer swelling measurements in pure solvents

The polymer was pre-weighed and immersed in a bottle containing the solvent, which was then sealed. The pre-weighed solvent was added at 5 times the weight of polymer. The samples were weighed, and the experiments were carried out at ambient temperature (typically 18 ± 2 °C). After being taken out of the sealed bottle the polymer sample was weighed, and then replaced in the bottle until the swollen weight reached equilibrium.

The swelling degree was measured for 5 samples, and the mean value was calculated. All measurements were expressed as the mean \pm standard error. Standard errors are equal to standard deviation divided by the square root of the sample numbers.

3.5 Swelling in solvent mixtures

3.5.1 Method

The swelling measurement followed the same method in Section 3.2.4., however in this case the mass and refractive index of the remaining mixture was measured. Solvent concentration in the remaining liquid was calculated from a calibration curve, and the

corresponding solvent concentration in the swollen polymer was calculated using a mass balance. The mass balance was based on equilibrium between polymer and solvent mixtures.

$$m_{is} + m_{ip} = m_{fs} + m_{fp} \quad (3.4)$$

where m_{is} is the mass of initial solvent mixture, m_{ip} is the mass of initial dry polymer, m_{fs} is the mass of final solvent mixture and m_{fp} is the mass of the final swollen polymer. The solvent equilibrium equation is given by:

$$m_{is}x_{is} + m_{ip}x_{ip} = m_{fs}x_{fs} + m_{fp}x_{fp} \quad (3.5)$$

where x_{is} is the concentration of solvent (wt%) in initial solvent mixture, x_{ip} (wt%) is the concentration of solvent in dry polymer, x_{fs} (wt%) is the concentration of solvent in remaining solvent mixture, and x_{fp} (wt%) is concentration in final swollen polymer. x_{ip} equals zero in the dry polymer, so Equation 3.5 becomes:

$$m_{is}x_{is} = m_{fs}x_{fs} + m_{fp}x_{fp} \quad (3.6)$$

Solvent concentration in the remaining liquid was calculated from the measured refractive index of the remaining solvent mixtures. It was then used to calculate equilibrium solvent concentration in the swollen polymer from the following equation.

$$x_{fp} = \frac{m_{is}x_{is} - m_{fs}x_{fs}}{m_{fp}} \quad (3.7)$$

3.5.2 Concentration measurement

Concentration measurement was based on the preparation of known solvent concentration and measurement of its refractive index. Calibration curves were prepared, and used for mass balance calculations.

The refractive index of a medium is the ratio of the velocity of light through a vacuum to the velocity of light through the medium. The solvent concentration was determined using

the refractive index (RI) measurement technique, which is based on the change in RI of a binary solvent mixture as a function of solvent concentration. Calibration tests were performed to assess the suitability of the RI method to determine binary mixture concentration for a range of mixtures. Experiments were performed using a refractometer (Mettler Toledo Refractometer 30PX) at a temperature of 20°C.

The refractometer that was available gave RI values that were accurate within (± 0.0002) based on repeat measurement of a single sample. In this case, the resolution of the technique was such that concentration of ethanol in hexane could be determined within 0.3%, ethanol in heptane within 0.6%, ethanol in water within 0.8%, and isopropanol in water within 0.6%. Figure 3-11 and 3-12 show the refractive index at different solvent concentrations.

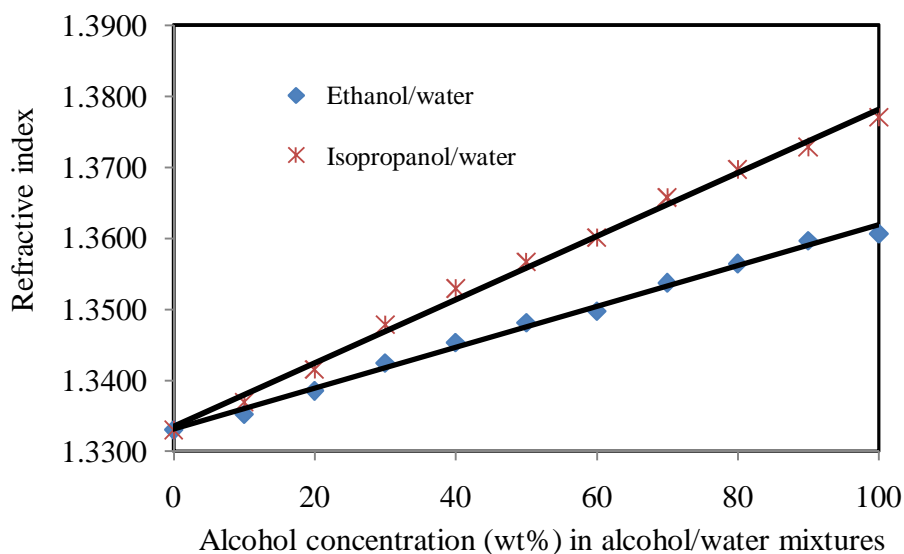


Figure 3-11 Refractive index plotted against alcohol concentration for ethanol/water and isopropanol/water mixtures

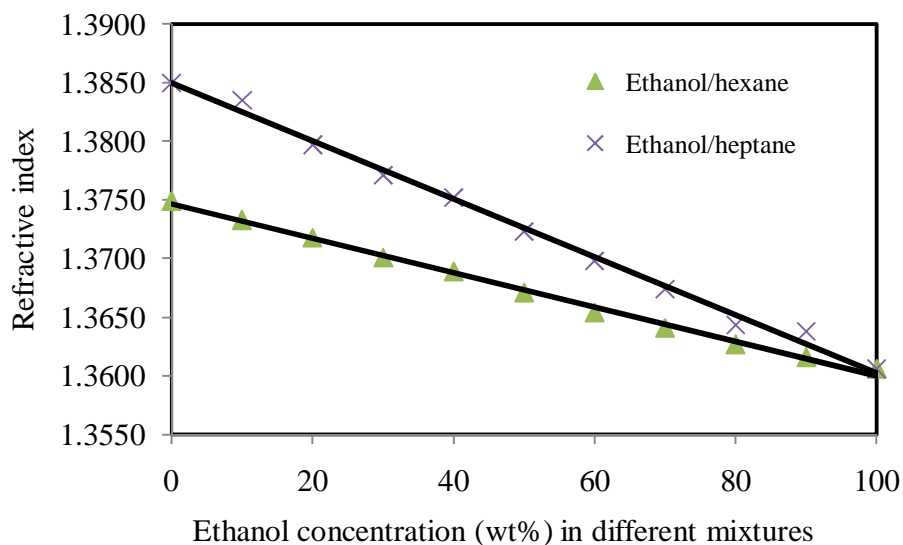


Figure 3-12 Refractive index plotted against ethanol concentration for ethanol/hexane and ethanol/heptane mixtures

The refractometer was calibrated with water on a weekly basis.

3.6 Effect of pressure on polymer swelling

3.6.1 Experimental apparatus

An experimental system was designed by the author to allow both the total swelling degree and the composition within the polymer to be measured when pressure was applied. A diagram of the apparatus is presented in Figure 3-13.

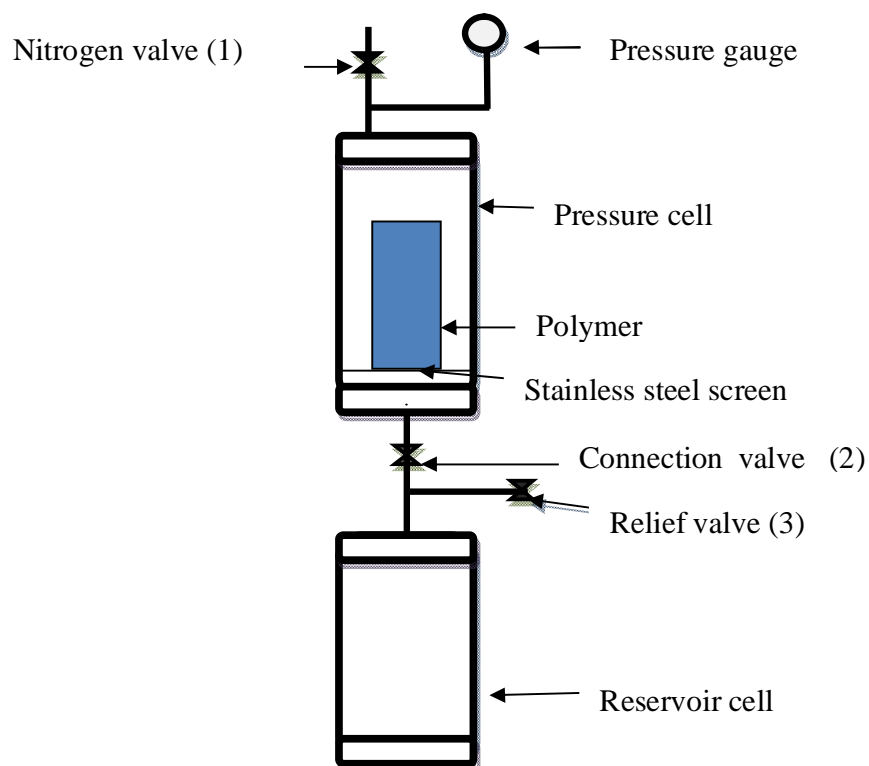


Figure 3-13 Schematic of the pressure cell and reservoir cell

The schematic in Figure 3-13 illustrates a novel apparatus which was used to measure polymer swelling at different applied pressure. The apparatus was composed of two parts: a pressure cell (capacity 300ml), and reservoir cell (capacity 300ml) (detailed design in Appendix 1). The strategy behind the apparatus design was to keep the swollen polymer under test pressure while the liquid was transferred to reservoir cell which did not allow the polymer to absorb more liquid when the cell was depressurized which is the advantage of this apparatus over existing systems.

3.6.2 Experimental procedure

The polymer was in the form of dense blocks, and was cast into a cylindrical shape and placed over the stainless steel screen plate in the pressure cell. The solvent was pre-

weighed and placed in the cell containing the polymer. The apparatus was assembled by connecting and sealing the two parts, and the force required to make this seal is generated by tightening the threads which attach the lower portion of the cell. The upstream side of the apparatus was connected by stainless steel tubing to a pressurised nitrogen supply. The operating pressure required for the pressure cell was induced using an oxygen-free nitrogen cylinder, and manipulated using a pressure regulator valve (1) capable of producing a maximum pressure of 25 bar. Nitrogen was applied to pressurise the upstream side of the apparatus, while the cell below it remained at atmospheric pressure. Pressure was varied from 0 to 20 bar over the liquid in the region above the polymer, and the apparatus left until equilibrium was reached. At the end of the experiment, valve (2) was opened to allow the solvent to be transferred to the reservoir cell, whilst maintaining the polymer at high pressure. The system was depressurised to atmospheric pressure slowly to avoid sudden decompression of the volatile solvent within the swollen polymer. Pressure release was attained using the relief valve (3). The experiments were carried out at ambient temperature.

3.6.3 Measurement method

The swelling measurement followed the same method detailed in Section 3.2.4, however in this case the pressure was varied over the polymer/liquid system. A mass balance between liquid, polymer and the experimental rig was established as expressed by Equation 3.8

$$m_{is} + m_{ip} + m_{rig} = m_{fs} + m_{fp} + m_{rig} \quad (3.8)$$

where m_{rig} is weight of the rig (220 g for the two cylinders, pipes and connections). The rig weight was constant, and rearranging Equation 3.8 gives Equation 3.7.

CHAPTER THREE EXPERIMENTAL

Polymer samples were prepared for swelling measurements according to the method detailed in Section 3.5. A piece of pre-weighed polymer was immersed in a flask containing solvent of known weight, which was present in large excess compared to the amount of polymer. The polymer was allowed to swell until it reached equilibrium, and was then transferred with its liquid to the pressure cell, where a set pressure was applied to the polymer and liquid. Swelling experiments in different solvents were performed under pressure.

The polymer was then removed from the cell and weighed. The rig filled with the liquid was weighed; mass of the liquid was calculated. A mass balance example for a sample of PDMS (8 g) swelled by n-heptane are shown in Table 3.3. In the case of solvent mixtures the refractive index of the remaining mixture was measured. The solvent concentration method followed the same procedures detailed in Section 3.5.

Table 3.3 Example of mass balance of pressure apparatus

Pressure (bar)	Swollen PDMS, m_p (g)	Solvent m_l , (g)	Mass of the rig, m_{rig} (g)	SD, (wt%)
0	27.28	50.00	220	241
20	26.00	51.28	220	225

Chapter 4 **POLYMER CHARACTERISATION**

4.1 Introduction

This chapter aims to characterize the pre-polymers RTV615A, RTV615B, as well as PDMS and PVA with different crosslinking contents. The first section presents the equipment and techniques used for the characterization of the polymers utilised in this study, Gel-permeation chromatography (GPC) and Attenuated Total Reflectance-Fourier transform Infrared spectroscopy (ATR-FTIR). The second section presents the results and analysis obtained from GPC and ATR-FTIR.

4.2 Equipment and method

4.2.1 Gel-permeation chromatography (GPC)

4.2.1.1. GPC Theory

GPC was used to monitor the molecular weights of polymers. In the operation of GPC, the polymer is dissolved in a solvent and passed through a column of highly porous material. This column consists of a hollow tube tightly packed with polymer beads (polystyrene) designed to have pores of different sizes. As the solution travels down the column, molecules larger than the pore size cannot enter the pores and elute together as the first peak in the chromatogram. Molecules that can enter the pores will have an average residence time in the particles that depends on the molecular size and shape. Different molecules therefore have different total transit times through the column as shown in Figure 3-1. This portion of a chromatogram is called the selective permeation region. Molecules that are smaller than the pore size can enter all pores, and have the longest residence time within the column and elute together as the last peak in the chromatogram. This last peak in the chromatogram determines the total permeation limit.

The retention time is compared to a standard molecular weight distribution to obtain molecular weight data for the sample.

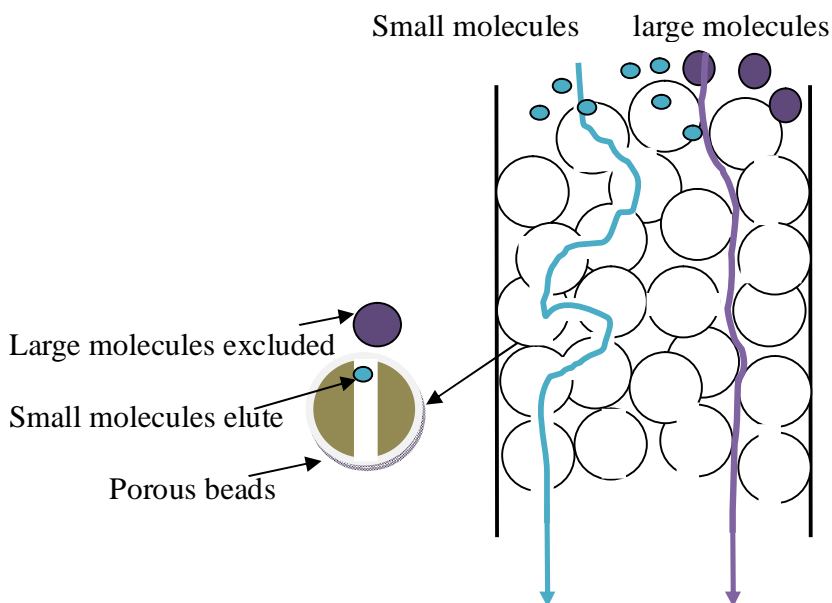


Figure 4-1 Schematic of a GPC column during operation

4.2.1.2. GPC equipment

The GPC measurements presented in this chapter were performed using PL-GPC-120 plus integrated GPC system fitted with mixed-D columns and a refractive index detector. The instrument was calibrated with polystyrene standards using Tetrahydrofuran (THF). GPC calibration curves were generated from 10 separate sample injections of each polystyrene standard. The exclusion limit is less than 12 minutes and permeation limit is over 18 minutes.

4.2.1.3 GPC output

GPC is used for determining the average molecular weight (M_n , M_w) and polydispersity (PDI) of polymer samples. M_n and M_w are different methods of identifying the average molecular weight of polymers (Equations 4.1 and 4.2).

$$M_n = \frac{\sum N_x M_x}{\sum N_x} \quad (4.1)$$

Where M_n is the number average molecular weight, and N_x is the number of moles whose weight is M_x .

$$M_w = \frac{\sum N_x M_x^2}{\sum N_x M_x} \quad (4.2)$$

Where M_w is the weight average molecular weight, and N_x is the number of moles whose weight is M_x .

The number average molecular weight (M_n) is a way of determining the molecular weight of a polymer. Polymer molecules, even ones of the same type, come in different sizes (chain lengths, for linear polymers), thus the average molecular weight will depend on the method of averaging. M_n is the ordinary arithmetic mean of the molecular weights of the individual macromolecules, and is determined by measuring the molecular weight of n polymer molecules, accumulating the weights, and dividing by n . The weight average molecular weight (M_w) is a way of determining the molecular weight of a polymer which gives more significance to longer chains. M_w is determined by accumulating the squared molecular weights of n polymer molecules, and dividing by the sum of the molecular weights. The PDI is determined by M_w/M_n and is a measure of the distribution of molecular mass in a polymer sample. It shows the distribution of individual molecular masses in a batch of polymers. The PDI has a value greater than 1, but as the polymer chains approximate a uniform chain length the PDI approaches unity [237].

4.2.2 Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).

4.2.2.1 ATR-FTIR theory

ATR-FTIR spectroscopy uses the infrared region to identify functional groups on a molecule. ATR-FTIR is a measurement technique whereby spectra are collected based on measurement of the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample. An infrared beam is directed into an optically dense crystal with a high refractive index. The internal reflectance creates a wave that extends beyond the surface of the crystal and into the sample held in contact with the crystal. This evanescent wave protrudes only a few microns ($0.5\ \mu\text{m}$ - $5\ \mu\text{m}$) beyond the crystal surface and into the sample. Consequently, there must be good contact between the sample and the crystal surface. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated or altered. The attenuated energy from each wave is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer. The infrared spectrum obtained then gives information on the molecular structure of the sample according to which energies were absorbed. Table 4.1 shows some of the wave numbers at which different bonds or functional groups respond. A schematic diagram of ATR-FTIR is presented in Figure 4-2.

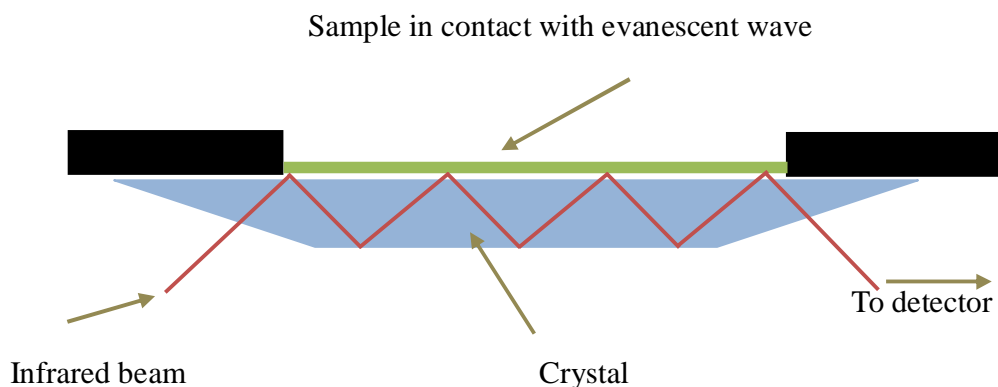


Figure 4-2 Schematic of ATR-FTIR during operation

Table 4.1 Functional groups and their corresponding wave numbers [238-239].

Functional group	Wave numbers (cm^{-1})
Siloxane group (-Si-O-Si)	1020-1100
Methyl-silicone groups (-Si-CH ₃)	800-1260-2960
Vinyl group(-CH=CH ₂)	1480
Hydrosilane group (-Si-H)	2060
Ether/acetal groups (-COC)	1097
Aldehyde group (-CHO)	1720
Methylene group (-CH ₂ -)	2940
Hydroxyl group (-OH)	3000-3600

4.2.2.2 ATR-FTIR equipment

A Nicolet 6700 ATR-FTIR spectrometer with ZnSe crystal was used in this study. The penetration depth of the infrared beam in samples ranged from 0.5 μm at 4000 cm^{-1} to 2 μm at 400 cm^{-1} for the ZnSe crystal with a 90° angle of incidence. For the technique to be successful, the following two requirements must be met:

1. The sample must be in direct contact with the ATR crystal, because the wave only extends beyond the crystal $0.5\ \mu\text{m}$ - $5\ \mu\text{m}$. This was achieved by a pressure arm that was positioned over the sample area and the applied force pushed the sample into the diamond surface.
2. The refractive index of the crystal must be significantly greater than that of the sample or else internal reflectance will not occur, and the light will be transmitted rather than internally reflected in the crystal. Typically, ATR crystals have refractive index values between 2.38 and 4.01. The majority of solids and liquids have much lower refractive indices [240].

4.3 Results and discussion

This section details the experimental results and analysis obtained from GPC and ATR-FTIR. GPC was used to monitor the molecular weight of RTV615A and RTV615B, but could not be used to identify the crosslinked polymers as they could not be dissolved in a suitable solvent. ATR-FTIR was used to identify the functional groups present in the polymer as well as the crosslinking reaction.

4.3.1 GPC for RTV615A and RTV615B

Samples were prepared by dissolving 20 mg of RTV615A or RTV615B in 0.7 mL THF. Figures 4-3 and 4-4 show the GPC analysis for RTV615A and RTV615B.

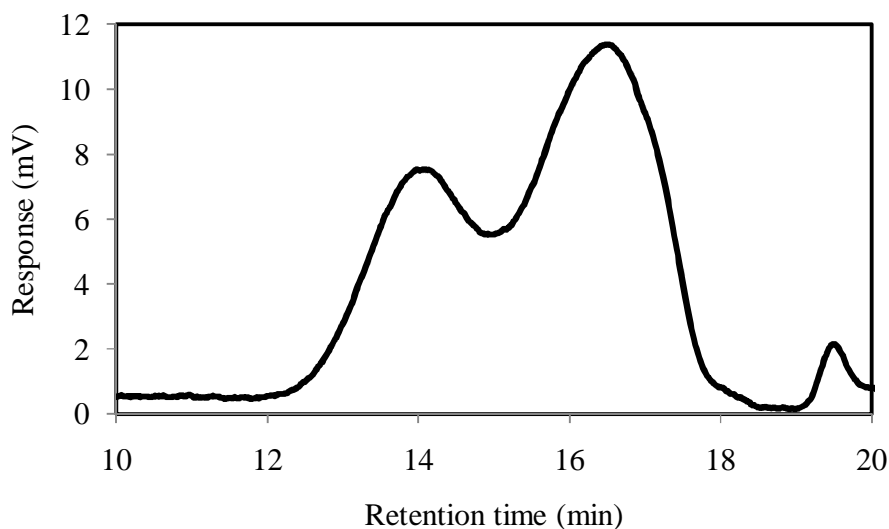


Figure 4-3 GPC for RTV615A (pre-polymer)

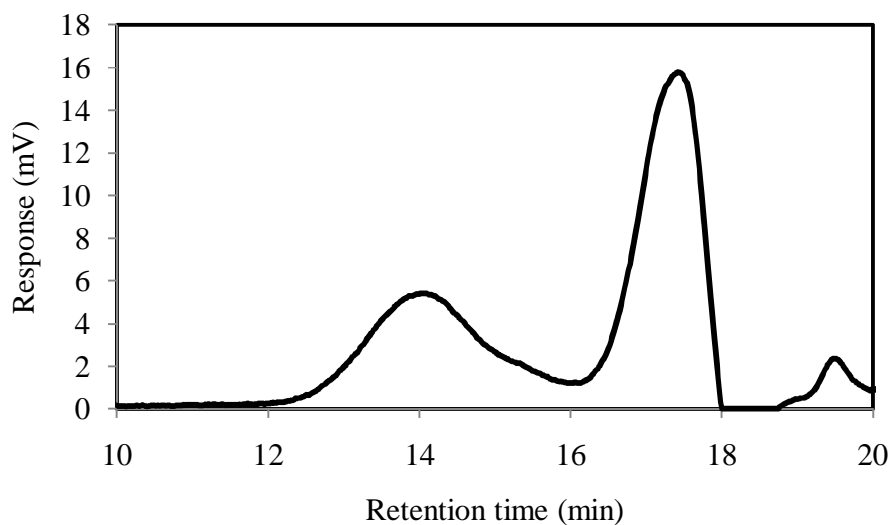


Figure 4-4 GPC for RTV615B (crosslinking agent)

Figure 4-3 and 4-4 present GPC analysis for RTV615A and RTV615B. It shows the distribution of polymer molecular weight at different retention times. The GPC trend for RTV615A exhibits a strong peak around 17 minutes, which corresponds to a number average molecular weight (M_n) of 4,509 g/mol, and a polydispersity index of 1.31. In the

chromatogram of RTV615A, there is a shoulder on the primary peak around 14 minutes, which corresponds to a number average molecular weight (M_n) of 61,031 g/mol and a polydispersity index of 1.15, which indicates the different molecular chains length, and the molecular weight distribution to identify the pre-polymer.

Figure 4-4 presents GPC analysis of the RTV615B. The trend has a bimodal character of molecular weight, which reveals that RTV615B has at least two chains lengths. The primary peak exhibits around 17 minutes corresponds to a molecular weight (M_n) of 1,723 g/mol, and a polydispersity of 1.19. The other peak around 14 minutes corresponds to a molecular weight (M_n) of 45,781 g/mol and a polydispersity of 1.35.

The results show that a widely differing molecular weight distribution for the pre-polymer and crosslinking agent was observed. It indicates that pre-polymer and crosslinking agent has a non-uniform chain length. The same results were observed by Stafie *et al.* [234] for GPC analysis of RTV615A and RTV615B. They found mainly a bimodal character for the crosslinking agent and indicate a wide molecular weight distribution. They suggested that different crosslinking degrees were obtained as a result of widely differing molecular weight of both the pre-polymer and crosslinking agent.

4.3.2 ATR-FTIR characterization

ATR-FTIR was used for the characterization of RTV615A, RTV615B, PDMS and PVA at various crosslinking content. Crosslinked samples were prepared and clamped against the face of the crystal. FTIR spectra of RTV615A and RTV615B are shown in Figure 4-5 and 4-6.

4.3.2.1 ATR-FTIR characterization for RTV615A and RTV615B

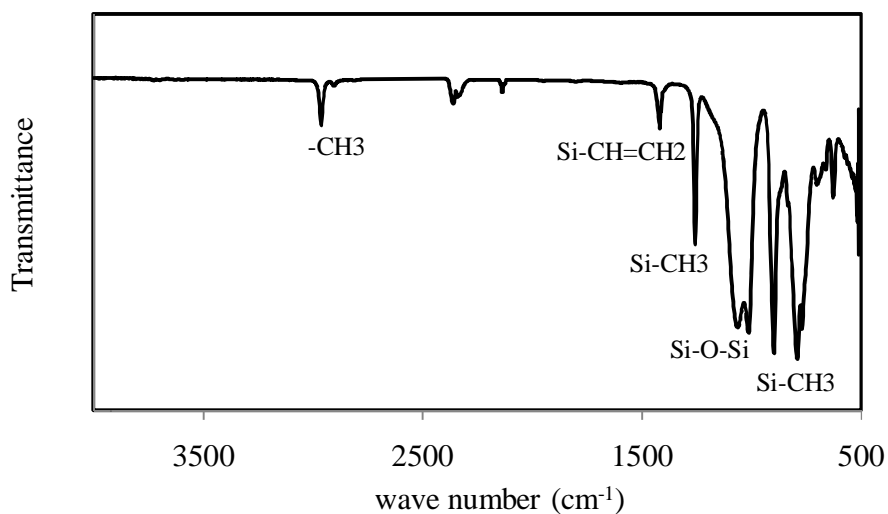


Figure 4-5 FTIR spectra of RTV615A

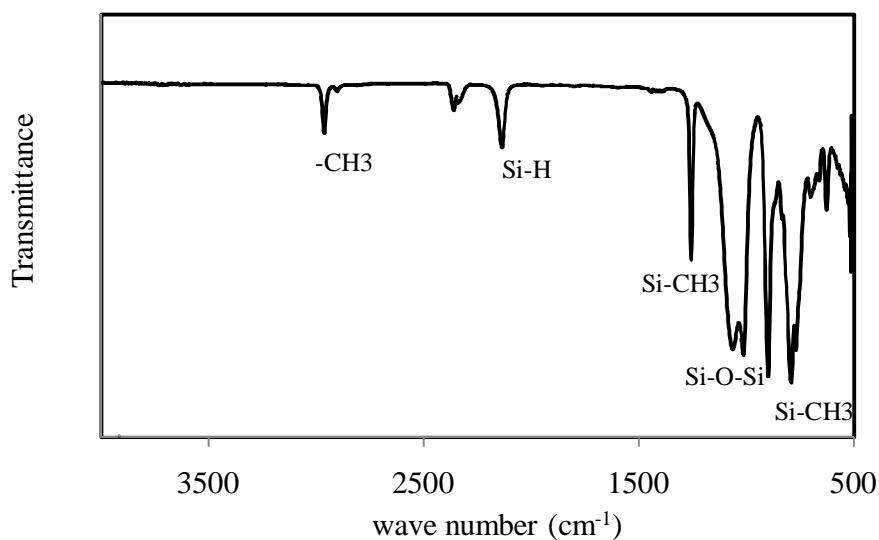


Figure 4-6 FTIR spectra of RTV615B

The infrared spectra of RTV615A is shown in Figure 4-5. The IR spectrum of RTV615A contains several expected peaks, which are siloxane group (Si-O-Si), methyl-silicone

groups (Si-CH_3), and vinyl group Si-CH=CH_2 [241]. Figure 4-6 presents infrared spectra of RTV 615B. The IR spectrum of the crosslinker contains groups similar to RTV615A. The absence of a vinyl group (Si-CH=CH_2) is observed and the addition of a Si-H, which acts as the functional crosslinker [176].

The FTIR spectra can be used to verify that RTV615A and RTV615B are both silicone components which contain the functional groups necessary to form crosslinked PDMS. The results indicate that no other additives were detected in either the pre-polymer or the crosslinker, and confirm the purity of the substances used.

4.3.2.2 ATR-FTIR for different crosslinked PDMS

ATR-FTIR spectra for different crosslinked PDMS were investigated. The results are shown in Figure 4-7.

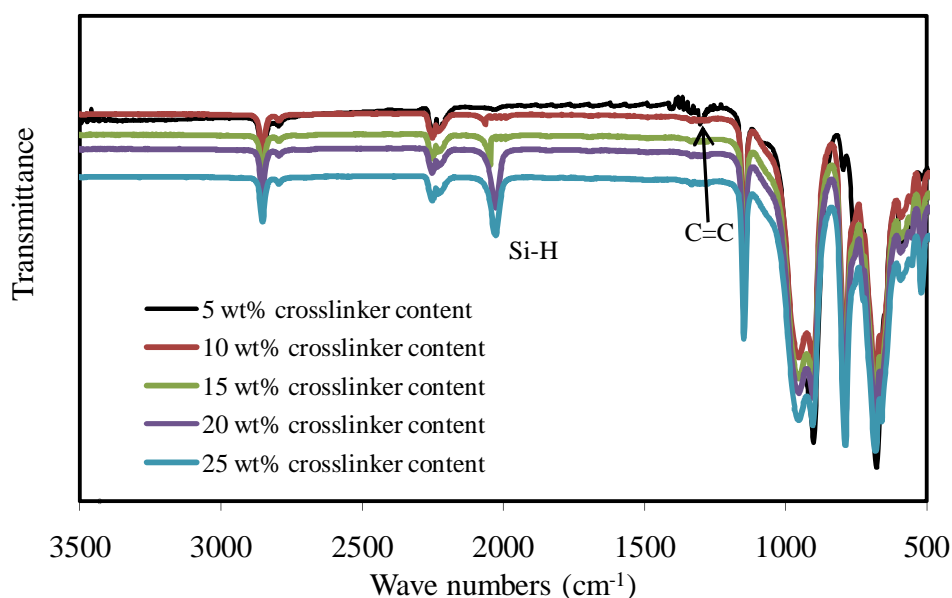


Figure 4-7 ATR-FTIR spectra of different crosslinked PDMS

The ATR-FTIR spectra contains several expected peaks which correspond to the pre-polymer and crosslinking agent (as described in Section 3.2.2). As explained in Section 3.2.2 the vinyl groups act as a crosslinking functional group in the pre-polymer, and the changes in the intensity of this peak can be attributed to the consumption of vinyl groups due to increasing crosslinking content. The spectra confirm that a hydrosilylation reaction occurs between Si-H groups at each end of the crosslinker, where it reacts with the C=C bond of the pre-polymers to obtain epoxidized PDMS. The IR spectrum for the PDMS samples prepared with a crosslinker content of 5% shows a peak at 1480 cm^{-1} , indicating an excess of vinyl groups still in the final polymer sample. For polymer samples prepared with 10, 15, 20, and 25% crosslinker content there are no apparent peaks at 1480 cm^{-1} , suggesting that the vinyl groups have completely reacted.

The Si-H absorption peak cannot be clearly detected for the polymer samples prepared at 5 and 10% crosslinker content. This indicates that all of the Si-H groups were consumed during the cross-linking reaction at these compositions. For 15, 20, and 25% crosslinker the changes in the intensity of Si-H groups were due to the addition of excess crosslinker, leading to an excess of Si-H groups in the final polymer samples after the crosslinking reaction.

Figure 4-7 shows that PDMS network is a blend of unreacted PDMS oligomers (still containing vinyl and/or Si-H groups) and fully-cured PDMS (without unreacted groups). The findings suggest that the addition of the crosslinker at concentrations at or below 10% leads to the existence of vinyl and/or Si-H groups in the PDMS network.

In order to investigate the degree of crosslinking this study deviated from the advice of the manufacturer, which was to use a 10/1 ratio of RTV615A/RTV615B [231]. The validity of this approach was investigated by characterising the resulting polymers using ATR-FTIR.

In order to quantify the different crosslinking content the peak areas of the hydrosilane group (-Si-H) at 2060 cm^{-1} , and the methyl-silicone groups (-Si-CH₃) at 2960 cm^{-1} were evaluated. The Si-CH₃ groups do not take part in the crosslinking reaction, therefore their peak areas were used as a standard [242]. However, the Si-H peak area increases with increasing crosslinker content, and this peak was used to verify the degree of crosslinking. The peak areas for RTV615A and RTV615B were evaluated before the crosslinking reaction took place. In RTV615A the Si-H peak area and Si-CH₃ peak area are 2.1 and 58.2 respectively, and the corresponding Si-H/CH₃ area ratio is 0.03. In RTV615B the ratio is 0.75. The crosslinking reactions reduce the peak area of Si-H in the final polymer, which can be calculated according to equation 4.3 [242].

$$\text{Crosslinked area} = Q_{\text{RTV615B}}(\text{crosslinking ratio}) + Q_{\text{RTV615A}}(1 - \text{crosslinking ratio}) \quad (4.3)$$

where Q is the ratio between the Si-H peak area and the Si-CH₃ peak area. The Si-H/CH₃ ratio obtained from FTIR was used in conjunction with Equation 4.3 to quantify the crosslinking content in the polymer as shown in Table 4.2.

Table 4.2 Peak area and ratio for PDMS of varying crosslinker content

Nominal crosslinking degree (wt%)	Area before crosslinking	Peak area at 2060 cm^{-1}	Peak area at 2960 cm^{-1}	Si-H/CH ₃ area ratio	Reduction in Si-H/CH ₃	Actual crosslinking degree (wt%)
5	6	1.2	301.0	0.0030	0.95	4.7
10	10	2.4	309.5	0.0070	0.93	9.4
15	14	6.3	315.2	0.0199	0.87	13.1
20	17	11.0	328.6	0.0335	0.82	16.4
25	21	18.0	396.5	0.0443	0.79	19.8

The data in Table 4.2 shows that increasing the crosslinker content from 5 to 25 % results in the corresponding crosslinking content in the PDMS increasing from 4.7 to 19.8 wt%. The results show that PDMS polymers prepared with 5 and 10% crosslinker contained a negligible amount of unreacted crosslinker in the final polymer. Polymers prepared at 15, 20 and 25% contained unreacted crosslinking agent and hence the polymer was a mixture of crosslinked PDMS and crosslinking agent. This result is in agreement with Lue *et al.* [242], who also used FTIR to verify the crosslinking content of PDMS. They concluded that PDMS made with 9 wt% crosslinking agent contained a negligible amount of unreacted crosslinker, whereas PDMS prepared with 20 wt% crosslinker resulted in a final polymer with 15 wt% crosslinking.

4.3.2.3 ATR-FTIR for different crosslinked PVA

In this study PVA samples were prepared from different ratios of crosslinker (GA) to the base PVAc. ATR-FTIR spectra for the different polymers are shown in Figure 4-8.

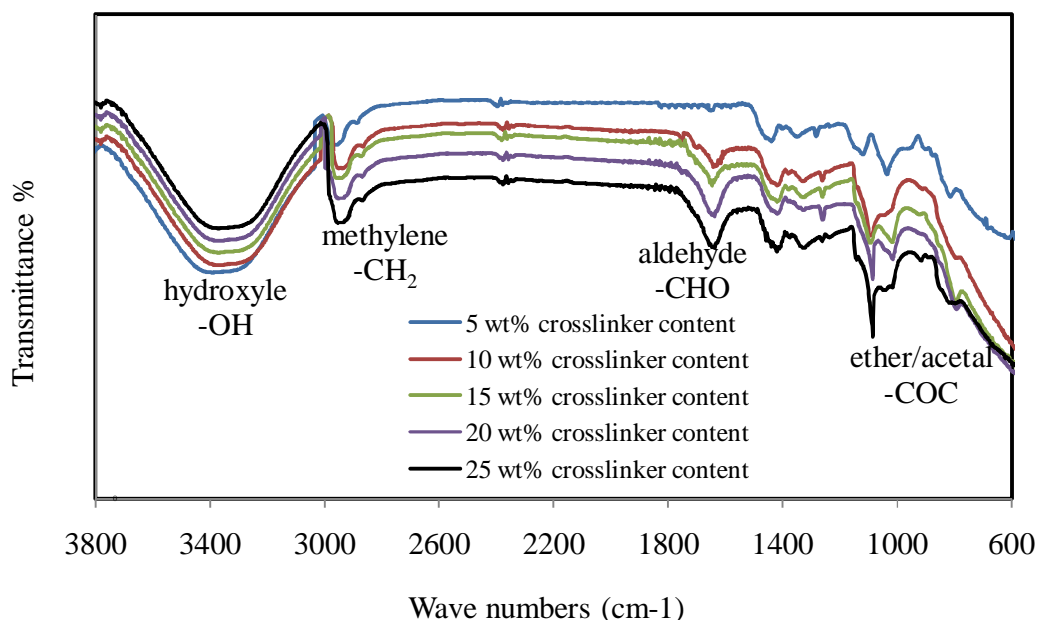


Figure 4-8 FTIR spectra for different crosslinked PVA

The IR spectra shows the corresponding groups such as ether/acetal (-COC), aldehyde (CHO-), methylene (-CH₂-), and hydroxyl (-OH) groups.

The appearance of the ether/acetal peak indicates that the acetylation reaction occurs between aldehyde and hydroxyl in the polymer. The appearance of aldehyde group corresponds to mono functional reactions (details in Section 3.3.2) [235, 243]. The IR spectra show the following three significant changes with increasing crosslinking content.

1. A decrease in hydroxyl groups from 5 to 25% crosslinked PVA. The spectral change results from the disappearance of the hydroxyl groups upon reaction with more aldehyde.
2. An increase in acetal ring and ether linkages as a result of the reaction between the hydroxyl groups and the aldehydes.
3. An increase in aldehyde peaks located at 1720 cm^{-1} , which is attributed to the increase in unreacted aldehyde in crosslinked PVA.

From the spectral changes in Figure 4-8, it can be seen that more hydroxyl groups are consumed and more acetal rings and ether linkages are formed as the crosslinker content increases. However, the increase in the aldehyde peak is unexpected. Therefore this set of aldehyde peaks can only be evidence for unreacted aldehydes of the two aldehyde groups in a GA molecule. Only one group participates in the reaction and is connected with a PVA chain while the other remains unreacted.

4.4 Conclusions

This study has shown that crosslinking was performed successfully for both PDMS and PVA. The degree of PDMS crosslinking was quantified by FTIR, the highest was 19.7% and the lowest was 4.7%. FTIR reveals that the PDMS network obtained using 10% RTV-615B is a network that contains negligible unreacted PDMS oligomers.

Although the pre-polymer and crosslinker was consumed during crosslinking reaction, FTIR has shown that the crosslinked polymer is composed of fully cured and unreacted polymer and by varying the ratio of pre-polymer and crosslinker, the crosslinked polymer have different characteristics.

Chapter 5 **SWELLING OF POLYMERS IN PURE SOLVENTS**

5.1 Introduction

The prediction of the separation characteristics of organic systems is very challenging since the physiochemical properties of solvents and their interactions with the membrane material significantly affect mass transport. Therefore, the evaluation of solvent/membrane interactions and swelling phenomena is necessary. Previous studies have shown the importance of membrane swelling in transport processes through NF membranes [64, 175].

Swelling is a thermodynamic phenomenon in which a solvent transfers from a liquid phase to a polymer phase, and deformation of the polymer network occurs as a result. The swollen material can be considered to be a mixture of solvent and polymer, and the thermodynamics of liquid mixtures can be extended to swollen polymers [244].

The evaluation of swelling in a wide range of solvents has been studied. For this purpose an experimental system was designed to measure swelling of both hydrophobic and hydrophilic polymers in solvents which exhibit a range of different polarities. All results are reported as wt%, unless otherwise stated. The swelling degree (SD%) was calculated based on Equation (3.3).

5.2 Polymer swelling in pure solvents

5.2.1 PDMS in pure solvents

Polymer samples were prepared for swelling measurements according to the method detailed in Section 3.4. The swelling degrees of PDMS in different solvents over time are shown in Figures 5-1 and 5-2.

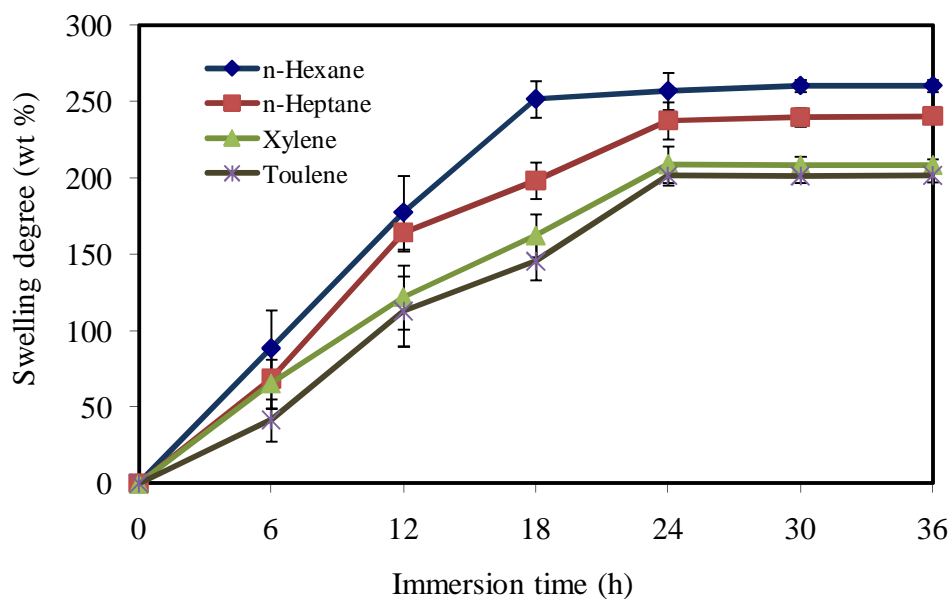


Figure 5-1 Swelling degree of PDMS in different solvents over time (Group 1).

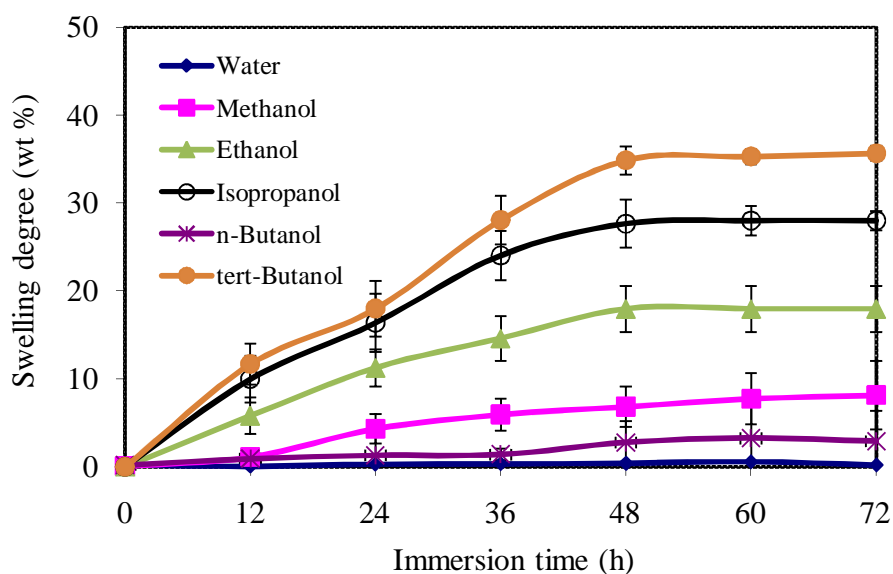


Figure 5-2 Swelling degrees of PDMS in different solvents over time (Group 2).

The swelling degrees illustrated in Figures 5-1 and 5-2 are the mean value of 5 samples. Errors bars were calculated as the standard deviation divided by the square root of the sample numbers, and indicate reproducibility of the experiments.

The solvents can be divided into two groups: group 1 includes n-hexane, n-heptane, xylene, and toluene, whose equilibrium swelling degrees are higher than 50% of the dry mass; these are shown in Figure 5-1. Group 2 includes isopropanol, ethanol, methanol, and n-butanol, tert-butanol, and water, whose equilibrium swelling degrees are lower than 50% of the dry mass; these are shown in Figure 5-2.

The time needed to reach the final swelling degree varies according to the solvent/polymer system. Figure 5-2 shows that swelling reaches a plateau for isopropanol, ethanol, methanol, and n-butanol, tert-butanol, and water after 48 hours. Figure 5-1 shows that plateau for n-hexane, n-heptane, xylene, and toluene occur after 24 hours.

Figure 5-2 illustrates that PDMS was swollen by isopropanol generating a mean swelling degree of 28.0%, while the corresponding values were 18.0% for ethanol, 9.0% for methanol, and 0% for water. Butanol has a 4-carbon structure, and the molecular formula is $C_4H_{10}O$, however it has different isomers with significantly different swelling behaviours. For example, n-butanol swells to 5.0%, while tert-butanol swells to 35%. From these results, the studied solvents ordered by swelling degree in PDMS are tert-butanol > isopropanol > ethanol > methanol > n-butanol > water. This indicates that in this group of solvents, tert-butanol has the strongest affinity with the polymer.

Figure 5-1 shows that PDMS was swollen by n-hexane, generating a mean swelling degree of 260%, while the values for n-heptane, xylene and toluene were 241%, 208 % and 201% respectively. From these results, the studied solvents ordered by swelling degree in PDMS are by n-hexane > n-heptane > xylene > and toluene. This indicates that in this group of solvents, n-hexane has the strongest affinity with the polymer.

5.2.2 PVA in pure solvents

The swelling experiments were extended to investigate the swelling of PVA, a hydrophilic polymer, in water, methanol, ethanol, isopropanol, n-butanol, and tert-butanol according to the method detailed in Section 3.4. Figure 5-3 shows the swelling degree of PVA in different solvents over time.

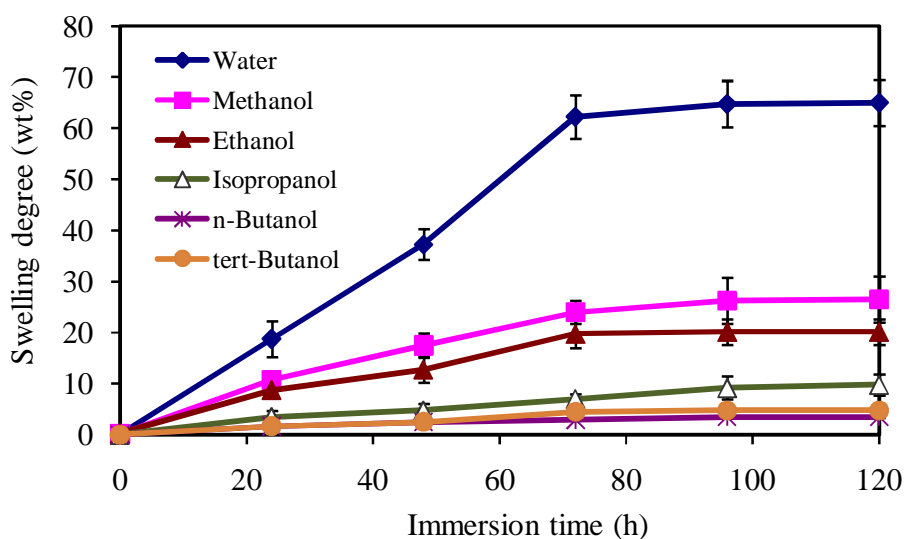


Figure 5-3 Swelling degree of PVA over time

The results clearly indicate that PVA immersed in water exhibits the maximum swelling degree, which then decreases for methanol, ethanol, isopropanol, and butanol, in that order. The swelling degree reaches a plateau for isopropanol, ethanol, methanol, n-butanol, tert-butanol, and water after 72 hours. The maximum swelling in water was 65%, while in methanol the value was 27.8%, 20.1% in ethanol and 9.5% in isopropanol. PVA has a different swelling degree in n-butanol and tert-butanol, as PVA swells in n-butanol to 3.5% and in tert-butanol to 4.7%.

5.3 Prediction of polymer swelling in different solvents

Several parameters can be used to assess the interaction between a polymer and a solvent, such as solubility and polymer-solvent interaction parameters.

5.3.1 Solubility parameter

Solubility parameters were used to assess the affinity of solvent molecules to the polymer material, and to give a systematic estimate of the compatibility between the two components.

The deviation between polymer solubility parameters and solvent solubility parameters ($\delta_p - \delta_s$) for PDMS 14.9 MPa^{0.5} and PVA 39.07 MPa^{0.5} [188], are shown in Table 5.1. The relationship between the absolute value of deviation between solvent and polymers solubility parameters and swelling degree of PDMS and PVA in various solvents is presented in Figure 5-4

CHAPTER FIVE SWELLING OF POLYMERS IN PURE SOLVENTS

Table 5.1 Solubility parameters of different solvents and deviation from polymers solubility parameter

Substance	δ_s (MPa ^{0.5})	$(\delta_s - \delta_{PDMS})$	$(\delta_{PVA} - \delta_s)$
Water	47.86	32.96	-8.79
Methanol	29.66	14.76	9.41
Ethanol	26.50	11.60	12.57
Isopropanol	23.60	8.70	15.47
n-Butanol	24.20	9.30	16.87
tert-Butanol	22.20	7.30	15.87
Xylene	18.20	3.30	-
Toluene	18.00	3.10	-
n-Heptane	15.20	0.30	-
n-Hexane	14.93	0.03	-

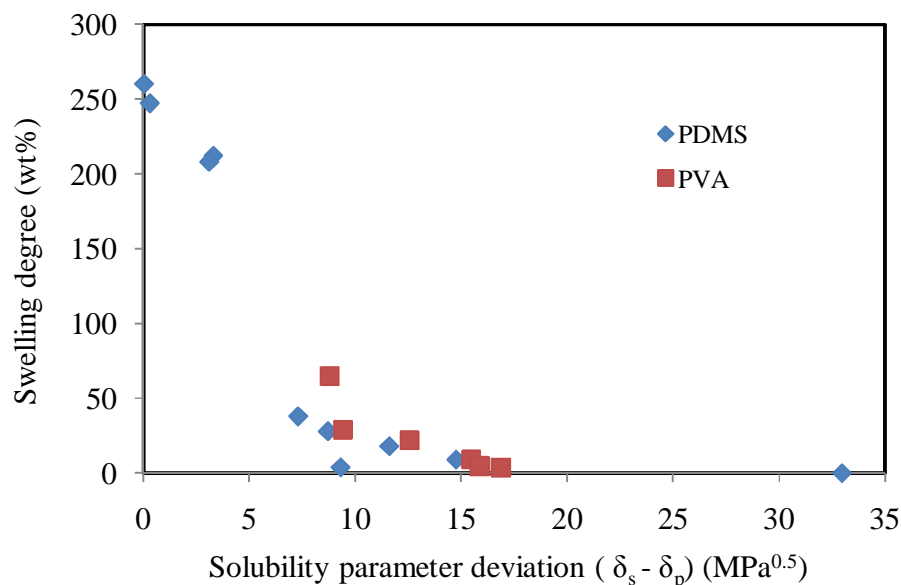


Figure 5-4 Relationship between swelling degree of PDMS and PVA in various solvents with the deviation between solvent and polymers solubility parameters

The results show that a greater degree of swelling is observed when the deviation between polymer solubility parameters and solvent solubility parameters ($\delta_p - \delta_s$) is close to 0, which indicates that solvents that have a value of solubility parameter similar to either of PDMS or PVA.

For PVA the minimum deviation ($\delta_p - \delta_s$) is 8.79 MPa^{0.5} with water, whereas for PDMS the minimum deviation ($\delta_p - \delta_s$) is 0.03 MPa^{0.5} with n-hexane. For example, the highest swelling degree is obtained with n-hexane, which deviates from that of PDMS ($\delta_p - \delta_s$) by 0.03 MPa^{0.5}. Whilst the lowest swelling degree is obtained with water which deviates from PDMS ($\delta_p - \delta_s$) by 32.96 MPa^{0.5}. For instance, PDMS is generally swollen by n-hexane 260.0%, n-heptane 241.0%, xylene 208.5%, and toluene 201.2%, isopropanol 28.0%, ethanol 18.0%, methanol 7.5%, and water 0; i.e. the swelling ratio increases with decreasing ($\delta_p - \delta_s$) values. n-butanol has a solubility parameter of 24.2 MPa^{0.5}, i.e. close in

value to PDMS solubility parameter ($14.9 \text{ MPa}^{0.5}$), but clearly does not follow the same trend as the other solvents. This may be attributed to the fact that solubility parameters do not take into account geometric aspects, such as size and structure of molecules (details in Section 5.3.2).

The results for PVA shows that a greater degree of swelling is observed with solvents that have a value of solubility parameter similar to that of PVA ($\delta = 39.07 \text{ MPa}^{0.5}$). For example, the highest swelling degree is obtained with water, which has a solubility parameter of $47.8 \text{ MPa}^{0.5}$ and deviates from that of PVA ($\delta_p - \delta_s$) by absolute value of $8.79 \text{ MPa}^{0.5}$. With increasing deviation the total swelling degree reduces. n-butanol has a solubility parameter of $24.2 \text{ MPa}^{0.5}$, which is closer to the solubility parameter of PVA than the solubility parameter of tert-butanol, which is $22.2 \text{ MPa}^{0.5}$. However, PVA swelling degree in n-butanol and tert-butanol shows non-linear behaviour, as PVA swells in n-butanol to 3.5% and 4.7% in tert-butanol.

The results clearly show that solubility parameter is useful for predicting the swelling behaviour of PVA and PDMS in solvents without knowing any other information about the solvents. Results show that the solubility parameter of the solvents influences swelling degree to an extent depending on deviation of solvent solubility parameter from PVA solubility parameter. However there are exceptions to the rule as demonstrated by butanol isomers.

The results show that the swelling degree of polymers is maximal when $(\delta_p - \delta_s)$ close to 0, where δ_p and δ_s are the solubility parameters of the polymer and solvent and swelling is minimum when the difference of $(\delta_p - \delta_s)$ has higher values. Although the Hildebrand-Scatchard equation (2.6) suggests that solvents with solubility parameter similar to that of PDMS ($14.9 \text{ MPa}^{0.5}$) or PVA ($39.07 \text{ MPa}^{0.5}$) will swell polymers effectively, the

relationship between solubility parameter and swelling is not linear and differs for each polymer-solvent system.

5.3.2 Different components of solubility parameter

The value of the solubility parameter is the sum of contributions of the numerical values assigned to the various structural groups. For example δ_r , polar interaction, δ_h , hydrogen bonds, and δ_d , dispersion forces from Equation 2.5. These components are shown in Table 5.2 for different solvents. With these values intermolecular interactions with other solvents, and also with polymers can be quantified [187]. The total swelling degree of PDMS and PVA at solvent component solubility parameters for each different solvents are plotted in Figure 5-5 and 5-6.

Table 5.2 Solvent solubility parameters and components accounting for polarity, dispersion and hydrogen bonding

Solvent	Solubility parameters MPa ^{0.5}			
	δ (MPa ^{0.5})	δ_r (MPa ^{0.5})	δ_h (MPa ^{0.5})	δ_d (MPa ^{0.5})
Water	47.8	16	42.3	15.6
Methanol	29.8	12.3	22.3	15.5
Ethanol	26.5	8.8	19.4	15.8
Isopropanol	23.6	6.1	16.4	15.8
n-Butanol	24.2	5.7	15.8	16.0
tert-Butanol	22.2	5.7	14.5	15.8
Toluene	18.2	1.4	2.0	18.0
Xylene	18.0	1.0	3.1	17.8
n-Heptane	15.2	0.0	0.0	15.2
n-Hexane	14.9	0.0	0.0	14.9

Table 5.2 shows different solvents with a range of solubility parameters spanning 14.9–47.8 MPa^{0.5}, which are based on δ_d , δ_r , and δ_h . Although the data shows a wide range of solvents, the dispersion parameter (δ_d) ranges from 14.9 to 18 MPa^{0.5} which indicates that δ_d is relatively similar across all the solvents studied. Therefore the discussion will focus on the influence of polarity and hydrogen bonding parameters. These values span a range of polarities, and thus potential swelling capability. For example, based on the numerical value of δ_h and δ_r for different solvents, polar solvents have higher levels of δ_h and δ_r , while for non-polar solvents, δ_h and δ_r are 0. The degree of polarity increases with increasing δ_r and δ_h of the solvents. Water is the highest polarity solvent, while n-hexane and n-heptane are non-polar solvents. In the case of alcohols the polarity decreases with increasing carbon number.

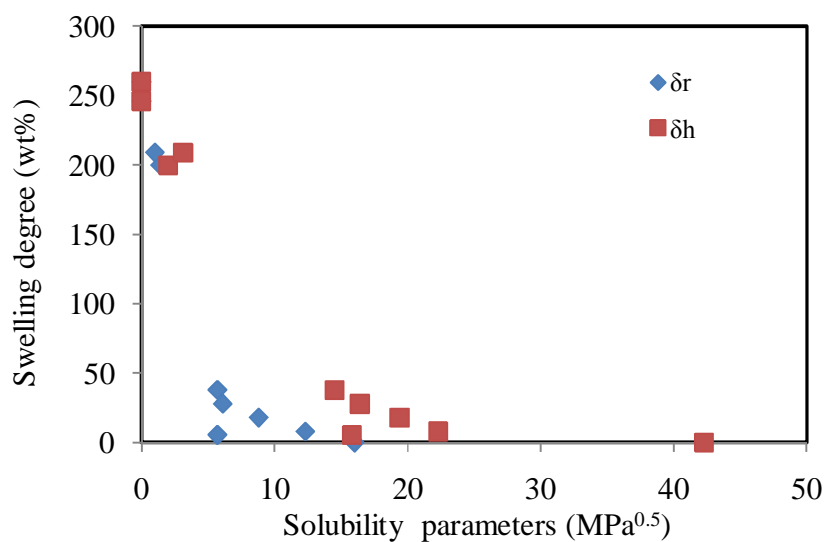


Figure 5-5 Relation between PDMS swelling degree, and δ_r , and δ_h for different solvents

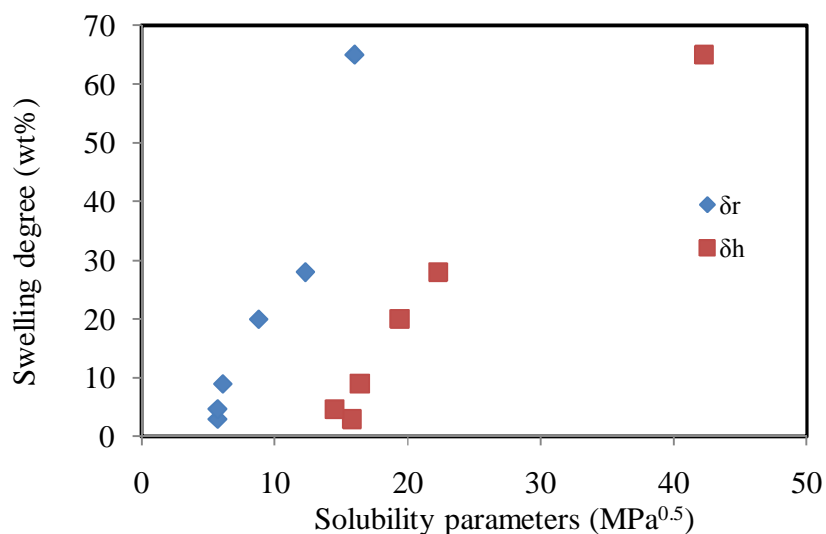


Figure 5-6 Relation between PVA swelling degree, and δ_r , and δ_h for different solvents

The results in Figures 5-5 and 5-6 show the effect of polarity and hydrogen bonding on the polymer swelling degree. The results indicate that the total degree of swelling is influenced by both polarity and hydrogen bonding parameters. For PDMS, the swelling degree decreases with increasing δ_r and δ_h of the solvents. However PVA swelling degree increases with increasing δ_r and δ_h .

One of the principal findings is that low polarity solvents exhibit the highest swelling degree with PDMS. The maximum swelling degree occurs in n-hexane, which is a non-polar solvent. However PDMS does not swell in water, which is the highest polarity solvent. As well as polarity the swelling degree is also influenced by molecular size and shape. It has previously been shown that size and shape play a key role in the transport of solute molecules in PDMS nanofiltration membranes [180, 182], and it is likely that a similar effect occurs with isomers of butanol. n-butanol swells to 5.0%, while the corresponding swelling degree in tert-butanol is 35.0%. This could be explained by the fact that n-butanol and tert-butanol compounds are structurally different. The OH group

connected to the first carbon in n-butanol makes it longer, and hence more difficult to absorb in PDMS. However, the OH group connected to the third carbon in tert-butanol results in a more compact structure which can more easily penetrate the PDMS network. The molecular size of n-butanol and tert-butanol are not equivalent, as n-butanol can be 35% larger than tert-butanol depending on the orientation, and the swelling degree given indicates that the smaller the solvent molecular size, the better the penetrating the polymer structure. Therefore, the molecular size of solvent is thought to play an important role in swelling degree, and this factor must also be considered in conjunction with the solubility parameter. The molecular dimensions of different solvents molecule were calculated from [245], and shown in Table 5.3.

Table 5.3 Molecular dimensions of different solvents

Solvent	Length (Å)	Depth (Å)	Width (Å)	Maximum dimension (Å)	Minimum dimension (Å)
Water	3.7	3.6	3.0	3.9	3.0
Methanol	5.2	4.5	4.2	5.2	3.8
Ethanol	5.0	5.1	6.4	6.4	4.9
Isopropanol	7.1	5.3	5.1	7.1	6.4
n-butanol	9.1	6.7	5.1	9.1	5.1
tert-butanol	6.6	6.1	5.7	6.6	4.1
n-hexane	10.3	5.1	5.0	10.3	4.1
n-heptane	12.9	5.1	5.1	12.9	4.1

Investigating PVA swelling degree in different solvents, the results indicate that the value of PVA swelling degree decreases from water > methanol > ethanol > isopropanol > tert-butanol > n-butanol, in this order.

The results indicate that increasing values of δ_r and δ_h lead to an increase in PVA swelling degree. For example, PVA has the highest swelling degree in water this could be attributed to the presence of water bonded with polymer free hydroxyl groups. PVA contains a large number of hydrophilic –OH groups, which can form hydrogen bonds with water and alcohols. In case of alcohol, the results indicate that the value of PVA swelling degree decreases with increase in carbon number which indicates that swelling degree is also influenced by molecular size and shape. The results conclude that the influences of polarity and hydrogen bonding parameters have a dominant role in determining the swelling degree. However the influence of dispersions parameter (δ_d) has a negligible influence in determining the polymer swelling degree for all solvents.

5.3.3 Polymer/solvent interaction parameter, χ

The swollen material can be considered to be a mixture of solvent and polymer, and the thermodynamics of liquid mixtures can be extended to swollen polymers. Therefore swelling values for a polymer in solvents can be used to obtain values of the interaction parameter. By using Equation 2.26 (Flory–Huggins equation) for the PDMS/PVA systems, the interaction parameters were determined for PDMS/PVA with solvent equilibrium data. The interaction parameter value is a factor that indicates the capacity of a polymer to be dissolved in a solvent. Numerically, if $\chi < 0.5$ for a polymer and solvent, this implies that the polymer and the solvent are completely miscible over the entire composition range [72]. This approach will be used to treat the experimental results obtained in PDMS/PVA swelling, and to predict the polymer solvent compatibility.

5.3.3.1 Different solvents in PDMS

The swelling degree of polymers in different solvents was used to calculate the solvent and polymer fractions in the swollen polymer. By using Equation 2.26, the interaction parameter was calculated based on the pure liquid activity (a_i) being equal to 1. As water does not swell PDMS, this interaction parameter could not be calculated. The interaction parameters for different solvents are presented in Figure 5-7.

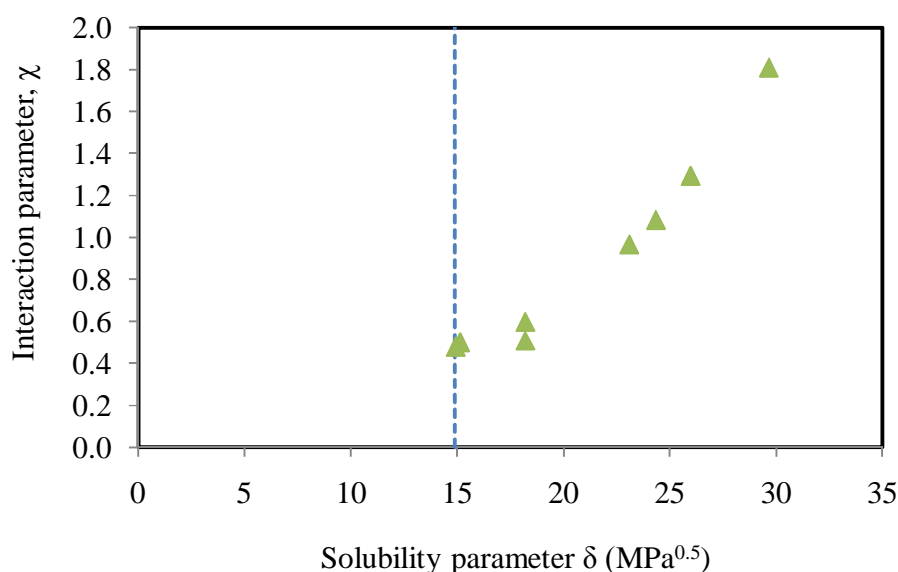


Figure 5-7 Solubility parameters of pure solvents versus polymer solvent interaction parameters of PDMS. The dashed line indicates the solubility parameter of PDMS ($\delta = 14.9 \text{ MPa}^{0.5}$)

The trend shows that lowest interaction parameter is 0.54 for n-hexane and the highest interaction parameter is 1.8 for methanol. The interaction parameter increases with increased solubility parameter of pure solvents. These results in agreement with the swelling results for these solvents, and indicates that the higher the swelling degree the lower the interaction parameter. The results show that the value of interaction parameters

could be used to identify the compatibility between polymer and solvent as well as δ_r and δ_h .

5.3.3.2 Interaction parameter for different solvents in PVA

PVA swelling data was used to calculate the interaction parameters for different solvents (as explained in Section 5.3.3) and results are presented in Figure 5-8.

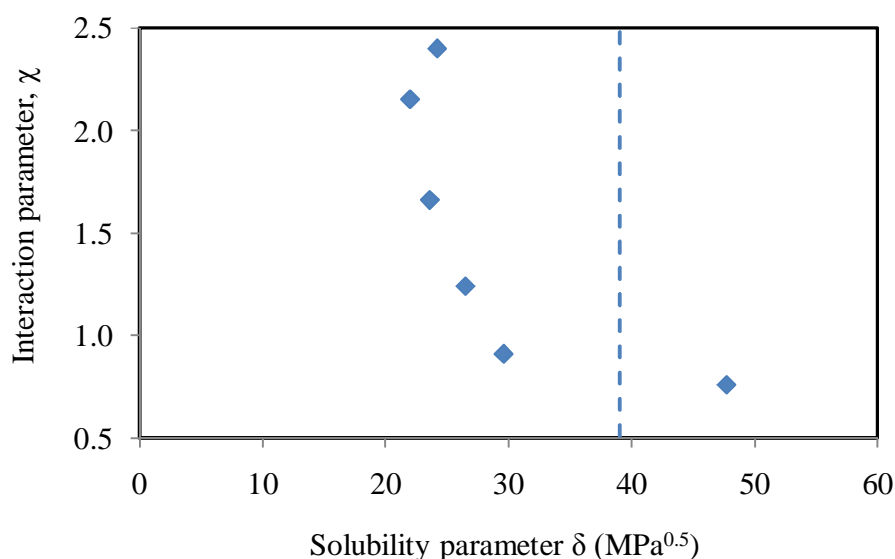


Figure 5-8 Solubility parameters of pure solvents versus PVA/solvent interaction parameters. The line indicates the solubility parameter of PVA ($\delta = 39.07 \text{ MPa}^{0.5}$).

The results show solubility parameters of solvents versus PVA/solvent interaction parameters and illustrate that the lowest interaction parameter is 0.7 for water and the highest is 2.4 for n-butanol and show that interaction parameter increase from water to n-butanol.

The results indicates that water is the most compatible of all solvents tested, because its polymer/solvent interaction parameter is the lowest value, while n-butanol is the least compatible.

These results agree with Han *et al.* [242], who studied the interaction parameter between PVA in water, and isopropanol. The interaction parameter was 0.7 and 1.6 for water and isopropanol respectively. They illustrated that the interaction between water and the membrane was greater than that between isopropanol and the membrane.

5.4 Conclusions

The results conclude that the total swelling degree depends on size and polarity of the solvents relative to the polymer. The highest swelling degree for PDMS was obtained with n-hexane and the lowest with water. The highest swelling degree for PVA was obtained with water and the lowest with tert-butanol.

Solubility parameter was used to predict the swelling degree and it was found that the deviation between polymer and solvent solubility parameter has a key role to predict the degree of swelling. Swelling is maximal when $(\delta_p - \delta_s)$ is 0. With increasing $(\delta_p - \delta_s)$ the swelling degree decreases and is minimal when the difference of $(\delta_p - \delta_s)$ has the highest value. This relationship is not linear and differs for each polymer-solvent system. The shape and molecular size must also be considered in conjunction with the solubility parameter to predict the swelling degree.

This study introduced a novel approach using solubility parameter components δ_d , δ_r , and δ_h , to gain further insights into the mechanism of swelling. Remarkable differences in the degree of swelling were obtained between δ_d , δ_r , and δ_h values. The data indicated δ_d has a negligible influence on the degree of swelling, while δ_r and δ_h have the dominant role in determining the swelling degree. The swelling degree was analysed using the Flory–Huggins equation, and the interaction parameters calculated for each polymer/solvent system, found to be in agreement with literature.

Chapter 6 EFFECT OF SOLVENT MIXTURES ON POLYMER SELECTIVITY

6.1 Introduction

One of the main hypotheses of this project is that the swelling behaviour of a polymer can be used to estimate the likely selectivity of a membrane made from that material. Swelling of PDMS and PVA in solvent mixtures was performed. Solvents of different concentrations were prepared, and their corresponding concentrations in swollen polymers were calculated based on a mass balance between swollen polymer and remaining solvent (see Section 3.5).

6.2 PDMS in ethanol/n-alkanes mixtures

Before selectivity was evaluated the effect of solvent mixture on the total swelling degree was investigated. PDMS samples were immersed in flasks containing ethanol/n-heptane and ethanol/n-hexane mixtures of known composition, and present in large excess compared to the amount of polymer. These mixtures have a wide span of polarity which ranges from non polar n-heptane/n-hexane to polar ethanol based, on the concentration of ethanol in the mixtures [246].

6.2.1 Total swelling degree

The total swelling degree was measured according to the method explained in Section 3.5. The influence of ethanol/n-heptane and ethanol/n-hexane mixtures on the swelling of PDMS is presented in Figure 6-1.

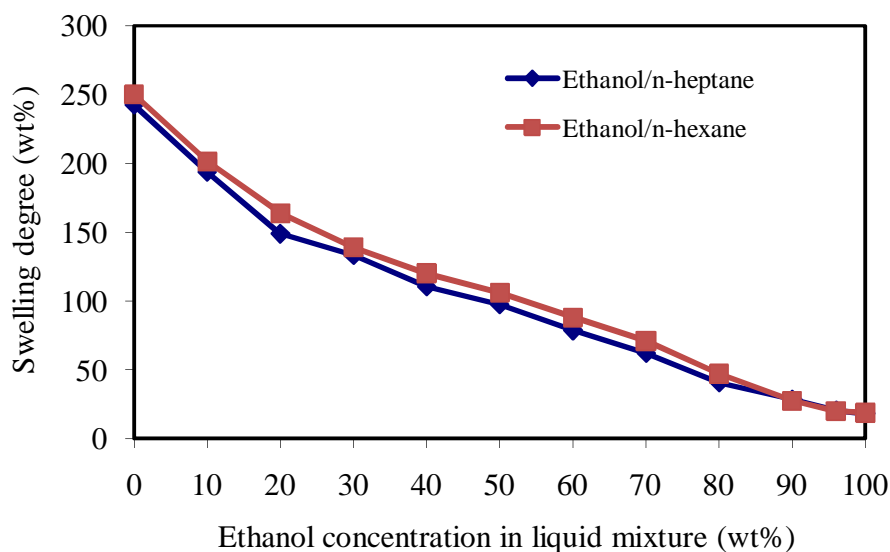


Figure 6-1 PDMS swelling degree over different ethanol concentrations in ethanol/n-alkanes mixtures

The results show that the swelling degree reaches a maximum value for n-alkanes and a minimum value for ethanol. At 0% ethanol, the swelling degree is maximal for both trends, while at 100% ethanol, the swelling degree is the lowest. The trends show that the mixtures swelled PDMS through the entire range of mixture composition, and that swelling degree decreases with increasing ethanol concentration. This is consistent with the swelling degree in pure solvents. From Figures 5-1 and 5-2, the swelling degree of PDMS in ethanol is 18%, compared with that 241% and 260% for n-heptane and n-hexane respectively.

6.2.2 Change in composition due to swelling

The degree of swelling reported in the previous section is only a measure of the overall uptake of the solvent in the polymer. This information is insufficient to evaluate whether and how the sorption of an individual component into the polymer is influenced by other

mixture components. The swelling equilibrium studies were also extended to investigate ethanol concentration inside the polymer as a function of the mixture compositions. The experimental method is explained in Section 3.5, and ethanol concentrations in the swollen polymers were calculated from a mass balance as shown in Table 6.2. The swollen polymer compositions of ethanol/n-heptane and ethanol/n-hexane mixtures are presented in Figures 6-2 and 6-3 respectively.

Table 6.2 Initial ethanol concentration and equilibrium ethanol concentration in swollen PDMS for ethanol/n-heptane and ethanol/n-hexane mixtures.

Ethanol concentration in liquid (wt%)	Ethanol concentration in swollen PDMS (wt%) for ethanol/n-heptane	Ethanol concentration in swollen PDMS (wt%) for ethanol/n-hexane
10	11.7	10.2
20	11.0	14.2
30	11.1	17.2
40	15.7	19.0
50	14.5	18.0
60	11.2	15.0
70	10.2	14.0
80	9.0	15.0
90	8.7	16.1

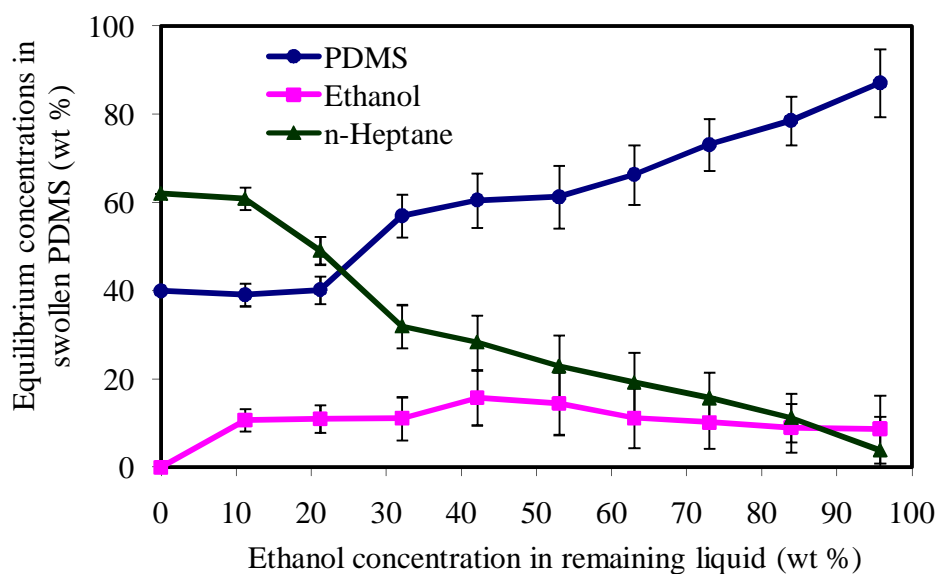


Figure 6-2 Equilibrium ethanol, n-heptane and PDMS concentration in swollen polymer at different ethanol concentrations.

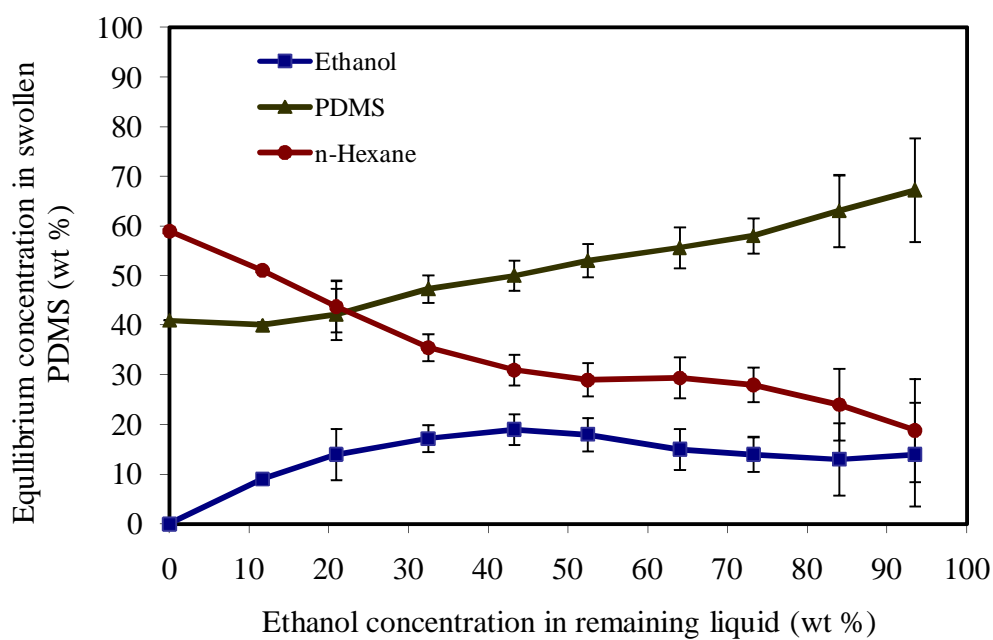


Figure 6-3 Ethanol, n-hexane and PDMS concentration at equilibrium in swollen polymer at different ethanol concentrations.

The results in Figure 6-2 and 6-3 demonstrate how the composition of the swollen polymer varies as the liquid composition changes. In Figure 6-2 the ethanol concentration within the liquid within swollen PDMS reaches a maximum of 15.7% at 42% ethanol whereas the other fractions of n-heptane and PDMS change more dramatically over the range of ethanol concentration.

In Figure 6-3 the ethanol concentration within the liquid in the swollen polymer reaches a maximum of 38% at 43% ethanol and the n-hexane concentration in the swollen polymer falls with increasing ethanol concentration. The results show that the amount of ethanol absorbed is less than n-heptane/n-hexane for PDMS at all alcohol concentrations. The contribution of PDMS can be excluded and the results interpreted in terms of the ethanol/n-alkane ratio, which is shown as a percentage in Figure 6-4.

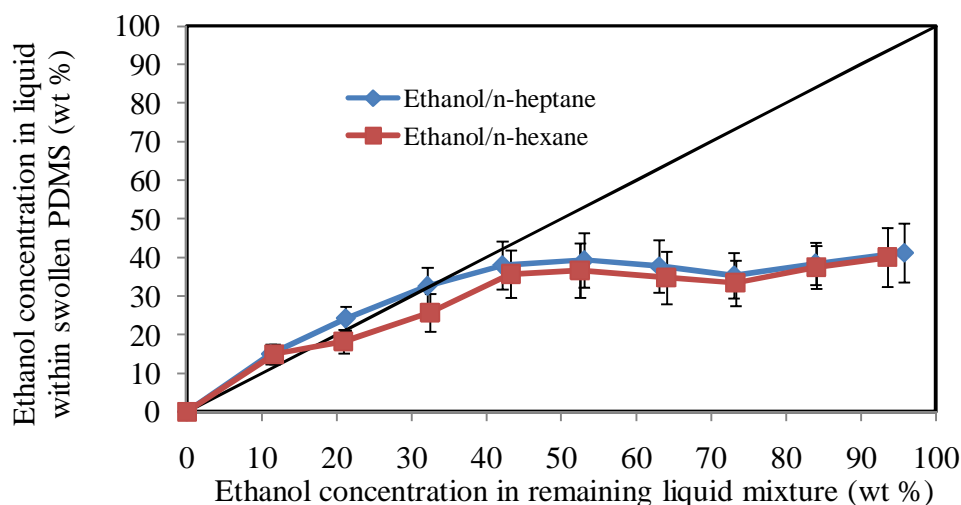


Figure 6-4 Ethanol concentration in liquid within swollen PDMS. The straight line ($y = x$) represents a selectivity of zero.

The results show how ethanol concentration within the liquid in the swollen polymer varies as the liquid composition changes. The selectivity of PDMS changes based on the

concentration. It is ethanol selective over n-heptane in the region of 0 to 17.2%, and ethanol selective over n-hexane in the region 0 to 38% ethanol. The selectivity of the polymer was evaluated by extended the results to calculate the sorption coefficient.

6.2.3 Sorption coefficient (K_i) of PDMS in ethanol/n-alkanes

Investigation of sorption coefficient requires ethanol concentration (C_{is}) in the liquid and the corresponding concentration (C_{ip}) within liquid in the swollen polymer. Sorption coefficients (K_i) were calculated from Equation 2.24 as a function of ethanol concentrations for ethanol/n-hexane and ethanol/n-heptane, and the results are presented in Figure 6-5.

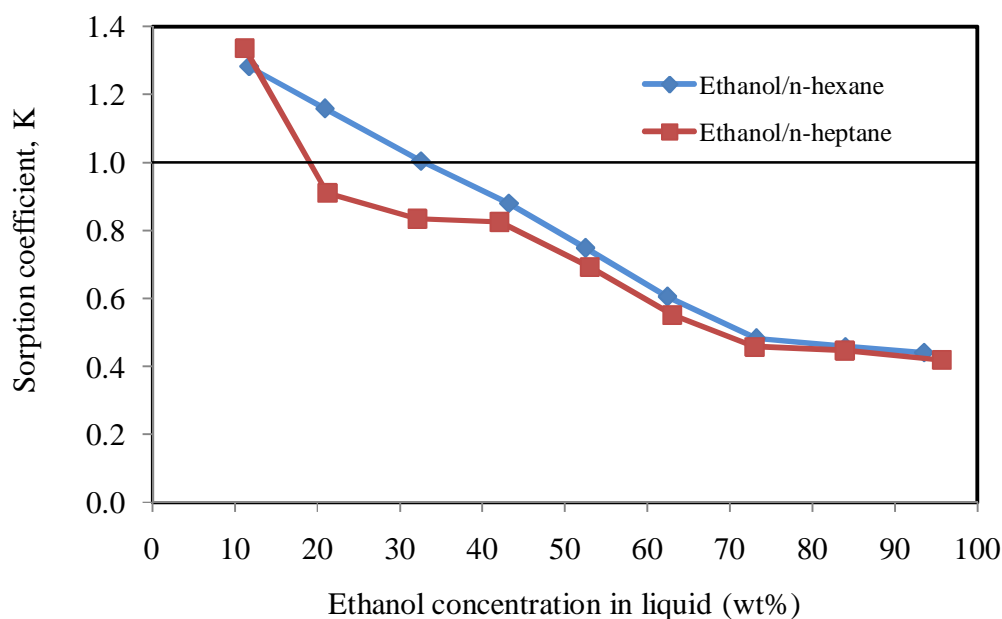


Figure 6-5 Ethanol sorption coefficient for ethanol/n-alkanes mixtures.

Similar trends are observed for sorption coefficient values in ethanol/n-heptane and in ethanol/n-hexane. The sorption coefficient has a maximum value of 1.33 and 1.28 at 11.7% and 11.2% ethanol in n-hexane and n-heptane respectively.

Increasing ethanol concentration leads to a decrease in the sorption coefficient, until it reaches around 0.4 at > 90% ethanol.

Figure 6-5 shows two regions; 0-18% ethanol in n-heptane and 0-32.2% ethanol in n-hexane are an ethanol-rich region in which the sorption coefficients are above a value of 1, which indicates that PDMS will be ethanol selective within this concentration range. The second region is n-heptane/n-hexane dominant, in which the ethanol sorption coefficients are lower than 1, and indicate that PDMS is n-heptane/n-hexane selective.

The results show a larger ethanol selective region with n-hexane compared with n-heptane. PDMS swells more in hexane, and it is thought that more ethanol can be absorbed into the PDMS via a mechanism governed by molecular size of the alcohol.

It is hypothesised that at low ethanol concentrations, n-heptane/n-hexane dominates the degree of swelling but ethanol can be absorbed as it is small, hence size is more dominant than polarity and the ethanol concentration in the swollen polymer is higher than that in the remaining liquid.

It is thought that at high ethanol concentration, ethanol dominates but n-heptane/n-hexane can be absorbed as polarity appears to dominate over size. Despite its hydrophobicity, and low value of δ (14.9 MPa^{0.5}) and it appears that ethanol is readily able to transfer into the PDMS despite being a low-swelling component.

The data in Figure 6-4 correlate with Figure 6-5, and show that the sorption coefficient decreases as total swelling degree decreases. This also indicates a mechanism dominated by molecular size. Whilst the mechanism is speculative at this stage it can be concluded

that sorption coefficients are highly dependent on the ethanol concentration, and PDMS can exhibit selectivity to either ethanol or n-heptane/n-hexane depending on the liquid composition.

6.2.4 Application of Flory-Huggins theory to the ternary system

The study was extended to investigate the ethanol activity inside the polymer, and how this varies with the liquid mixture in contact with polymer. Since selectivity depends on the concentration in the liquid, the aim of this section is to explore whether this behaviour can be predicted.

Flory-Huggins models were used to evaluate the ternary system. Since volume fractions, interaction parameters, and solvent molar volumes are known, the application of Equation 2.27 to calculate the ethanol activity in the polymer is possible.

The ethanol activity in the polymer was compared to the ethanol activity in liquid to check the validity of the Flory-Huggins theory. The activity coefficient in the liquid was calculated by the Van Laar method for liquid mixtures using equations 2.32, and 2.34 [228]. Ethanol activity values were calculated as a function of ethanol concentration and compared to those calculated using the Flory-Huggins model, and the results are plotted in Figures 6-6 and 6-7.

6.2.4.1 Determination of χ_{S1S2} interaction parameters

Ethanol/n-alkane interaction parameters (χ_{S1S2}) were calculated using published Vapour Liquid Equilibrium (VLE) data [247]. Ethanol activity was applied to Equation 2.30 in order to determine χ_{S1S2} for ethanol/n-alkanes mixtures. Table 6.3 shows values of interaction parameter for ethanol/n-heptane and ethanol/n-hexane.

Table 6.3 Interaction parameter ethanol/n-heptane and ethanol/n-hexane at different ethanol concentration.

Ethanol concentration (wt%)	$\chi_{\text{ethanol/n-heptane}}$	$\chi_{\text{ethanol/n-hexane}}$
10	1.70	1.81
20	1.54	1.72
30	1.38	1.62
40	1.24	1.54
50	1.15	1.47
60	1.14	1.47
70	1.31	1.59
80	1.92	2.03
90	4.14	3.68

From Table 6.3 it is apparent that χ_{s1s2} does not have a constant value, and changes with different ethanol fractions in ethanol/n-heptane and ethanol/n-hexane mixture. The average interaction parameter is used with Flory-Huggins equations for the ternary system to evaluate the ethanol activity in the swollen polymer [220]. The average interaction parameters are $\chi_{\text{ethanol/n-heptane}} = 1.72$ and $\chi_{\text{ethanol/n-hexane}} = 1.88$.

6.2.4.2 Predicted ethanol activity by application of Flory-Huggins theory

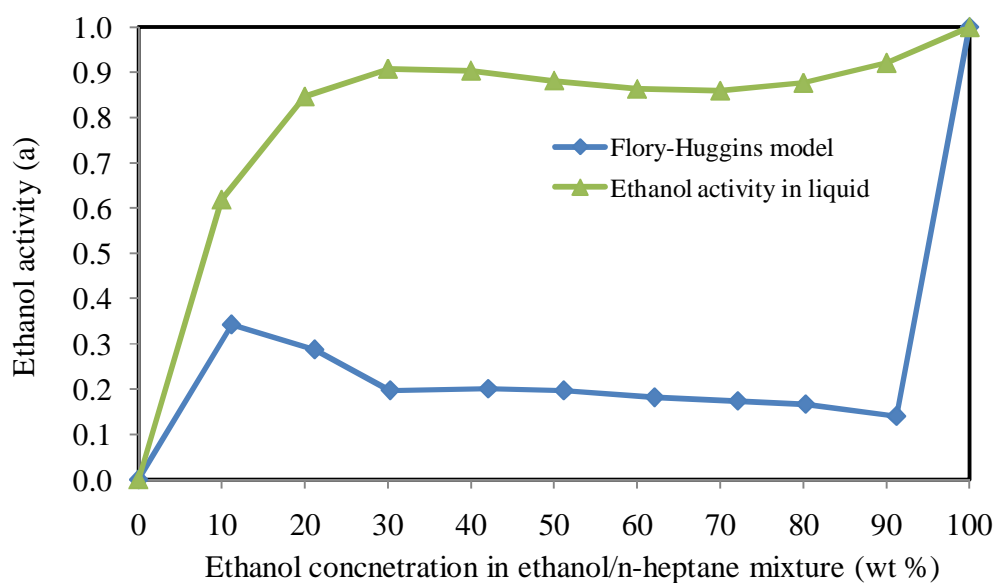


Figure 6-6 Ethanol activity in liquid and ethanol activity calculated using the Flory-Huggins model, at different ethanol concentration.

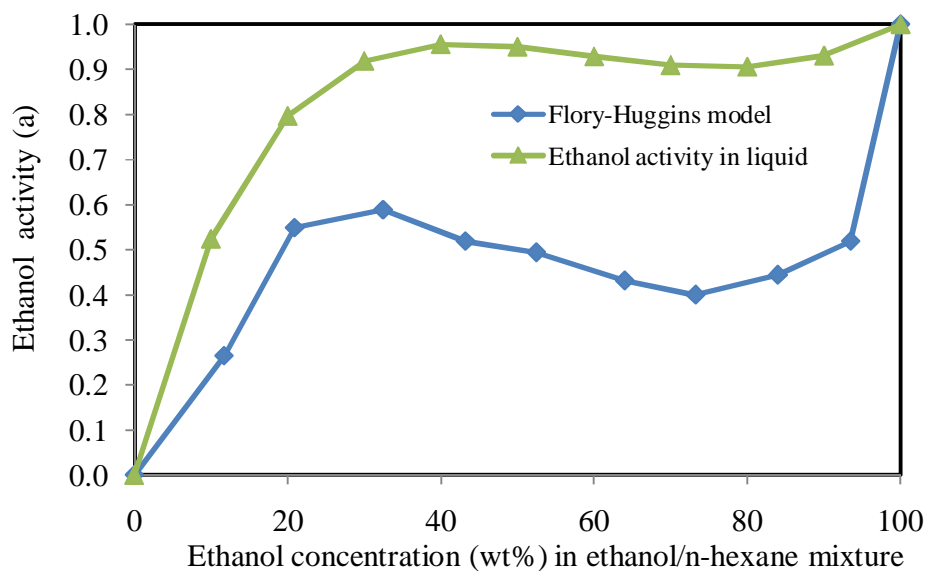


Figure 6-7 Ethanol activity in liquid and ethanol activity calculated using the Flory-Huggins model, at different ethanol concentration.

The results indicate that the ethanol activity predicted by the Flory-Huggins model is lower than the actual ethanol activity in the liquid, except for the case of pure ethanol and pure alkane. From Figure 6-6, at 11.2% ethanol, the predicted ethanol activity in PDMS has a maximum of 0.3. At higher concentration the activity declines until it reaches a minimum value at 0.14 (95.6% ethanol). At higher concentration up to pure ethanol the activity increases. The actual ethanol activity obeys a similar trend, with a peak at 40% ethanol, a trough at 80% ethanol and the highest value for pure ethanol.

The data for ethanol/n-hexane in Figure 6-7 follow the same trend as in Figure 6-6. The Flory-Huggins model under-predicts the activity, however the theory and experimental data show peaks and troughs at consistent ethanol concentrations, albeit with different values for activity. The results show poor consistency between ethanol activities in the swollen polymer calculated using the Flory-Huggins model and the actual ethanol activity in liquid. Quantitative prediction of ethanol activity in the swollen polymer could not be achieved by the Flory-Huggins model. A constant polymer/solvent interaction parameter was assumed, which is consistent with the approach used by [220], which may explain the limitation of the Flory-Huggins model in this case.

6.3 Sensitivity analysis

In order to investigate the effect of average value of χ_{s1s2} on the applicability of the Flory-Huggins model in ethanol/n-heptane, 3 values of χ_{s1s2} were selected from Table 6.3 and applied to Flory-Huggins model.

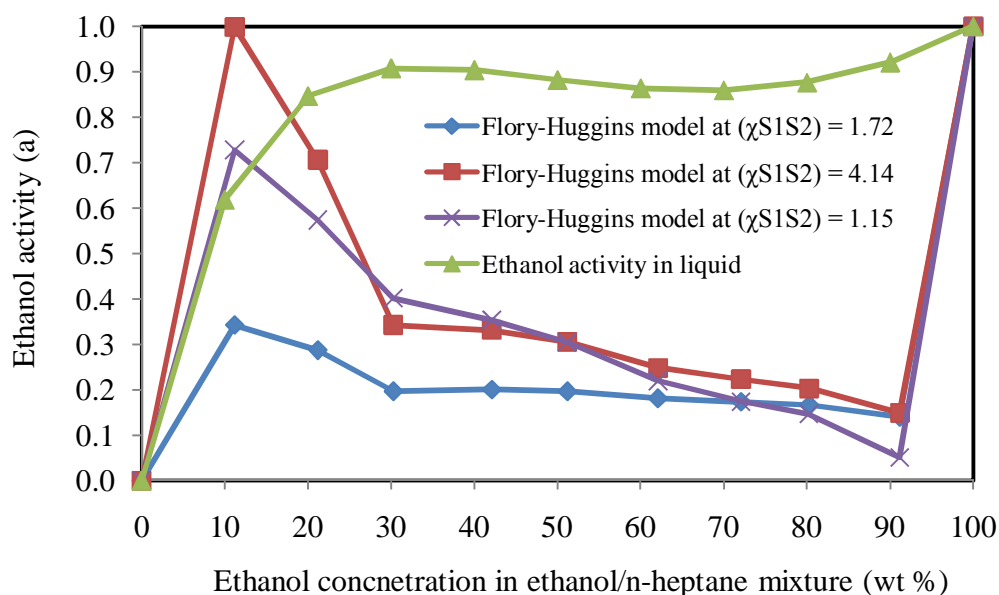


Figure 6-8 Sensitivity analysis of the Flory-Huggins model

The results indicate that the ethanol activity predicted by the Flory-Huggins model is lower than the actual ethanol activity in the liquid, except for the two cases of $\chi_{s1s2} = 4.14$ and $\chi_{s1s2} = 1.15$ from 0 to 27% ethanol and from 0 to 12%. The results show the maximum ethanol activities are in the range from 0 to 20% for ethanol/n-heptane mixtures.

At low ethanol concentrations the predicted values are closer to the experimental data, however when ethanol concentration is above 20% the Flory-Huggins model does not match the actual ethanol activity. At higher concentration the activity declines until it reaches a minimum value at 0.14 (95.6% ethanol).

The results show that the parameter χ_{s1s2} is not the sole reason behind the limitation of the Flory-Huggins model, and the physics which underpin the theory require more detailed investigation.

6.4 PDMS in alcohol/water

6.4.1 Total swelling degree

PDMS was subjected to different alcohol/water concentrations to determine the swelling degree. The influence of these mixtures on swelling is presented in Figure 6-9.

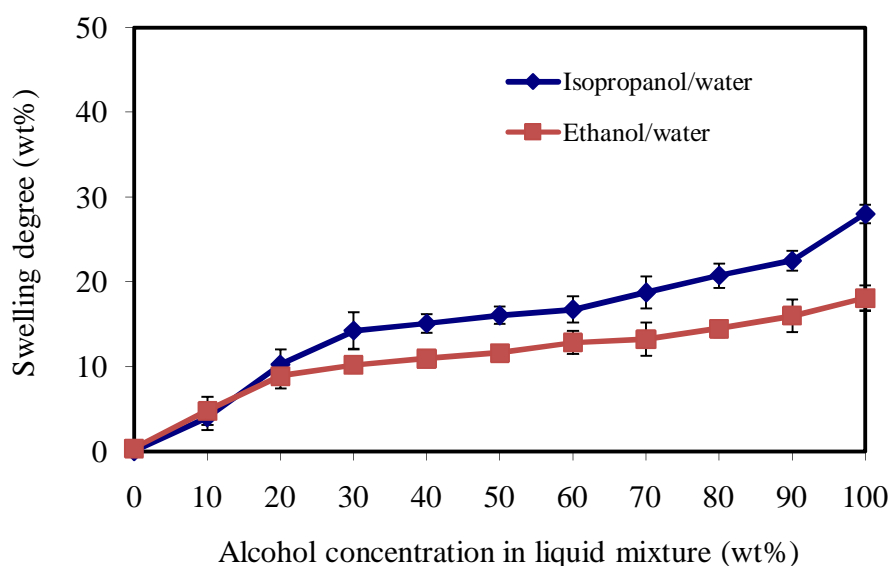


Figure 6-8 Swelling degree plotted against alcohol concentration in alcohol/water mixtures

The results show that swelling degree varies as the liquid composition changes. It is apparent that the swelling degree range is very narrow compared with the alcohol/alkane mixture, however the PDMS swells throughout the entire range of mixture composition. The swelling degree for isopropanol/water mixtures is higher than that for ethanol/water mixtures, which is consistent with the swelling degree observed in pure solvents. From Figure 5-1, the swelling degree of PDMS in ethanol and isopropanol are 18% and 28% respectively, compared with 0% in water.

The results also show that the degree of swelling rises with increasing alcohol concentration, which is expected on the basis that alcohol swells the polymer and water

does not. In this case it is expected that polymer swelling is due to the existence of the alcohol component in the mixture since water does not swell PDMS.

6.4.2 Change in composition due to swelling

The composition of isopropanol and ethanol in the swollen polymer were calculated as described in Section 3.5, and results are shown in Table 6.4. The swollen polymer compositions of isopropanol/water and ethanol/water mixtures are presented in Figures 6-10 and 6.11 respectively.

Table 6.4 Alcohol concentration, equilibrium ethanol and equilibrium isopropanol concentration in swollen PDMS.

Alcohol concentration (wt%)	Ethanol concentration in swollen PDMS (wt%)	Isopropanol concentration in swollen PDMS (wt%)
10	4.8	4.7
20	8.9	10.2
30	11.2	14.2
40	12.2	15.1
50	12.2	16.0
60	12.7	16.7
70	13.2	17.5
80	14.5	18.2
90	16.0	20.7

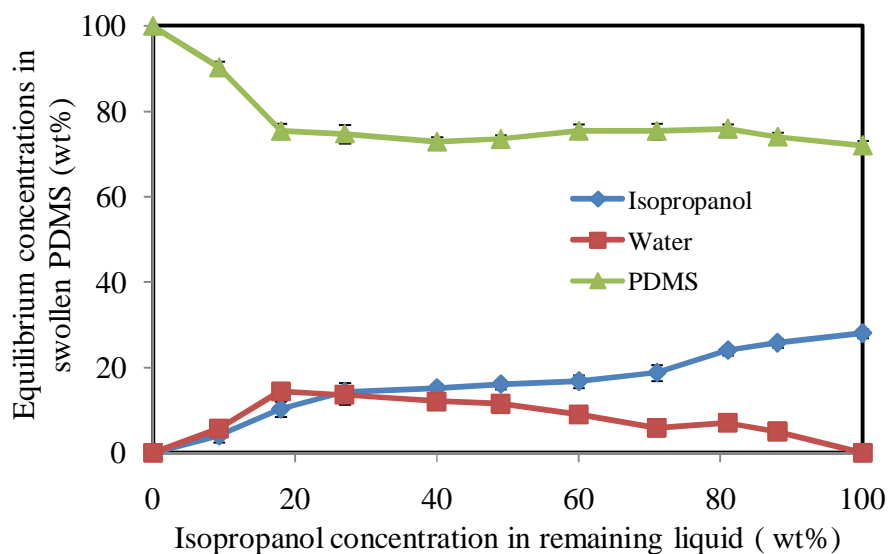


Figure 6-9 Relationship at equilibrium between isopropanol, water, and PDMS concentrations in the swollen polymer.

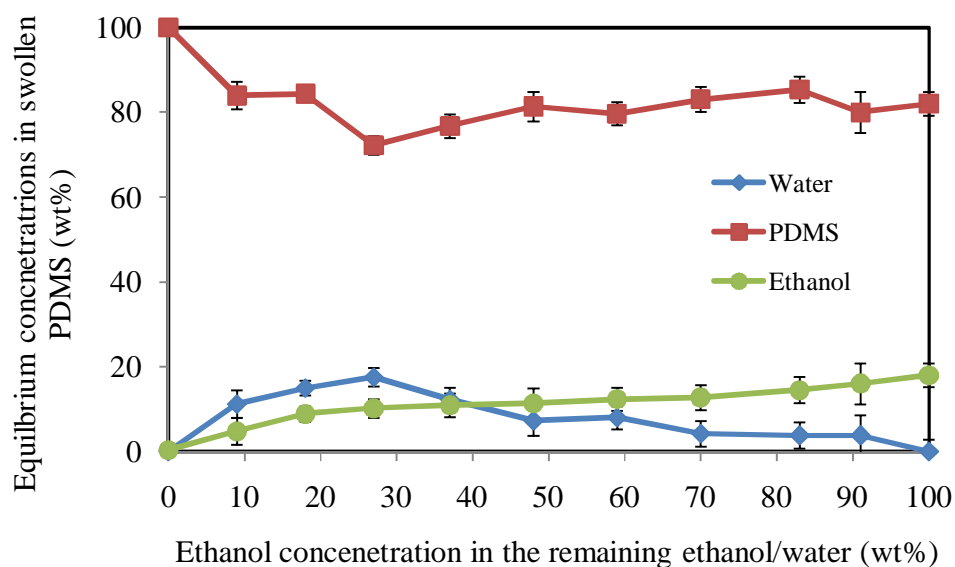


Figure 6-10 Relationship between ethanol, water, and PDMS concentrations at equilibrium in the swollen polymer.

The results show that the composition of the swollen polymer changes as the liquid composition changes. They also show that water is present in significant quantities within the swollen polymer, despite PDMS exhibiting no swelling with pure water, indicating that the alcohol/water system is behaving the same manner as the alcohol/n-alkanes system.

Figure 6-10 shows the isopropanol concentration increases progressively in the swollen polymer with increasing isopropanol concentration in the liquid. The water concentration increases to a maximum value of 14% at 18%. At 27% isopropanol both water and isopropanol concentrations in swollen PDMS are the same at 14.4%. The results in Figure 6-11 show ethanol concentration in swollen PDMS increases over the entire concentration range. Water exhibits a maximum of 16.5 at 27% ethanol, the same concentration at which isopropanol exhibited a maximum in Figure 6-10.

PDMS absorbed a quantity of water, which is relative to the alcohol concentration. It is thought that the polarity and corresponding solubility parameter of the mixture is in between that of water and alcohol. The data shown in Figure 6-10 and 6-11 include the contribution of PDMS to the composition of the swollen polymer, hence the alcohol and water concentrations are low. However, to assess the likely selectivity of the polymer the results can be extended to study the alcohol/water ratio, i.e. the composition of the liquid within the swollen polymer phase, as shown in Figure 6-12.

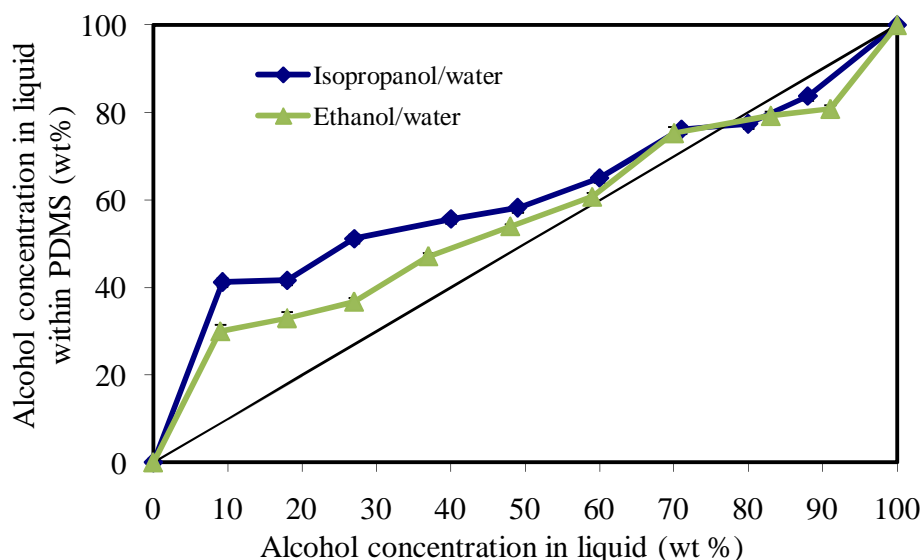


Figure 6-11 Alcohol concentration in the polymer plotted against the equilibrium concentration in the liquid phase. The straight line ($y=x$) represents a selectivity of zero

The results show that alcohol concentration within the liquid in swollen PDMS increases with increasing ethanol concentration in the liquid phase. The data also show that the isopropanol concentration is higher than that of ethanol from 0 to 70% alcohol in the liquid. PDMS appears to be alcohol selective over water in the region from 0 to 78.9% alcohol. However, increasing ethanol from 78.9 to 100%, PDMS is likely to be selective towards water, and it appears that water is readily able to transfer into the PDMS despite being a low swelling component. This could be due to the size of water molecules in relation to ethanol and isopropanol. At high alcohol concentration the PDMS network is swollen with relatively large free volume. Despite its large value of δ ($47.8 \text{ MPa}^{0.5}$), it appears that water is able to selectively absorb at high concentrations. It is proposed therefore that for low water concentration, the molecular size dominates over polarity.

The trend shows that equilibrium ethanol/water in swollen PDMS is similar to VLE for alcohol/water in distillation where azeotropes exists at 95.6% ethanol and 88% isopropanol. This data show similar behaviour to azeotropes, where the concentration of alcohol cannot be enriched above 78.9% using PDMS.

Comparing these results to Figure 6.4, the alcohol/water system has a different profile to alcohol/n-alkane systems. At low concentrations the alcohol concentration in the swollen polymer is higher than that in liquid for the alcohol/water system. PDMS is highly alcohol selective up to 70% alcohol in ethanol/water mixtures. For ethanol/alkane mixtures the ethanol concentration in the swollen polymer is higher than that in liquid up to 17.2% (n-heptane) and 38% (n-hexane), much lower concentrations than with the alcohol/water system.

The sorption mechanism for both systems is governed by a combination of size and polarity. At low ethanol concentrations in water the degree of swelling is low but ethanol is preferentially absorbed. It is thought that the mechanism in this case is dominated by polarity since ethanol molecules are larger than water molecules. At higher ethanol concentrations the degree of swelling is larger and more water is absorbed as in this case it appears that size dominates over polarity.

6.4.3 Sorption coefficient (K) in alcohol/water mixtures

The alcohol sorption coefficient in swollen PDMS was calculated based on the swelling data and the results are presented in Figure 6-13

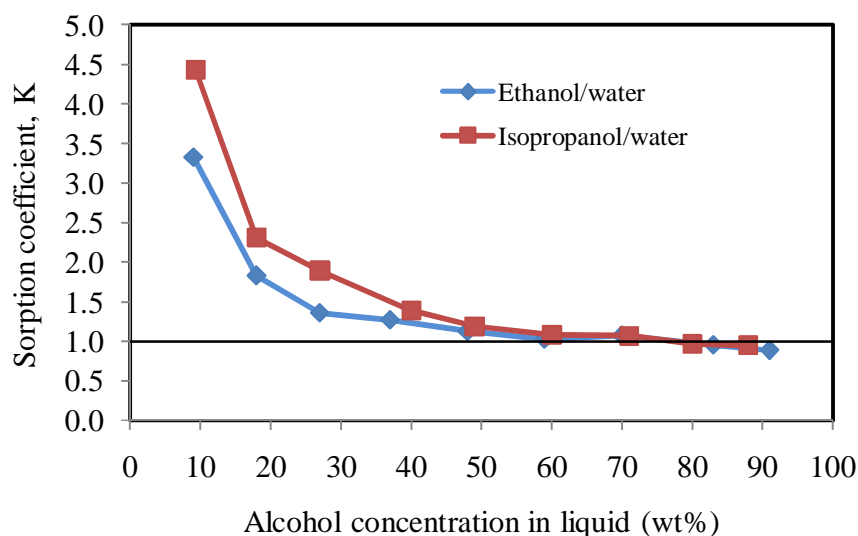


Figure 6-12 Alcohol sorption coefficient at different alcohol/water mixtures

Figure 6-13 indicates that a non-linear relationship exists between sorption coefficient and alcohol concentration, with similar trends observed for ethanol/water and isopropanol/water mixtures. The alcohol selective region in which the sorption coefficient values are over the value of 1, is clearly observed from 0 to 78.9 wt% alcohol. With increasing alcohol concentrations the sorption coefficient decreases below 1 where PDMS is selective towards water. For alcohol concentration from 0 to 60% sorption coefficients for isopropanol are higher than that for ethanol, whereas at high alcohol concentrations the sorption coefficients are similar. The data indicate that PDMS is highly selective at low alcohol concentrations, where K values > 3 are obtained. The results suggest that for the case of alcohol dehydration, where there is a low concentration of alcohol that needs to be separated from the water, PDMS polymer may be used as a membrane to preferentially permeate alcohol and reject water. This could make PDMS a good candidate material to recover alcohol from wastewater streams where it is relatively dilute. However for high

alcohol concentration, PDMS will be much less effective as the sorption coefficient is much lower. If alcohol is to be purified above 78.4% then PDMS cannot be used due to the presence of zero selectivity regions, similar to azeotropes in distillation. For alcohol/water mixtures the flux will be very low, however lower flux can be partly compensated by improving the membrane structure, i.e. reducing the effective thickness of the membrane or increasing the membrane surface area [177].

6.4.4 Application of Flory-Huggins theory to ternary system

6.4.4.1 Determination of χ_{S1S2} interaction parameters

Interaction parameters were calculated using published VLE data [248]. Alcohol activity was applied to Equations 2.30 and 2.31 in order to determine χ_{S1S2} for alcohol/water mixtures. Alcohol/water interaction parameters (χ_{S1S2}) were calculated as described in Section 6.3.4.1.

Table 6.5 Alcohol/water interaction parameter χ_{S1S2} at different alcohol concentrations

Alcohol concentration (wt%)	$\chi_{isopropanol/water}$	$\chi_{ethanol/water}$
10	1.99	1.06
20	1.40	0.82
30	1.04	0.64
40	0.83	0.54
50	0.73	0.51
60	0.74	0.59
70	0.85	0.81
80	1.14	1.35
90	1.96	2.99

It is apparent that $\chi_{\text{isopropanol/water}}$ and $\chi_{\text{ethanol/water}}$ are not constant. The interaction parameter is taken as average [220] for use with Flory-Huggins equations to evaluate the alcohol activity in the swollen polymer. The average values are 1.03 and 1.19 for ethanol/water and isopropanol/water respectively.

6.4.4.2 Predicted isopropanol activity from Flory-Huggins theory

A comparison between actual alcohol activity and predicted activity calculated by the Flory-Huggins model for isopropanol/water and ethanol/water are presented Figure 6-14 and 6-15.

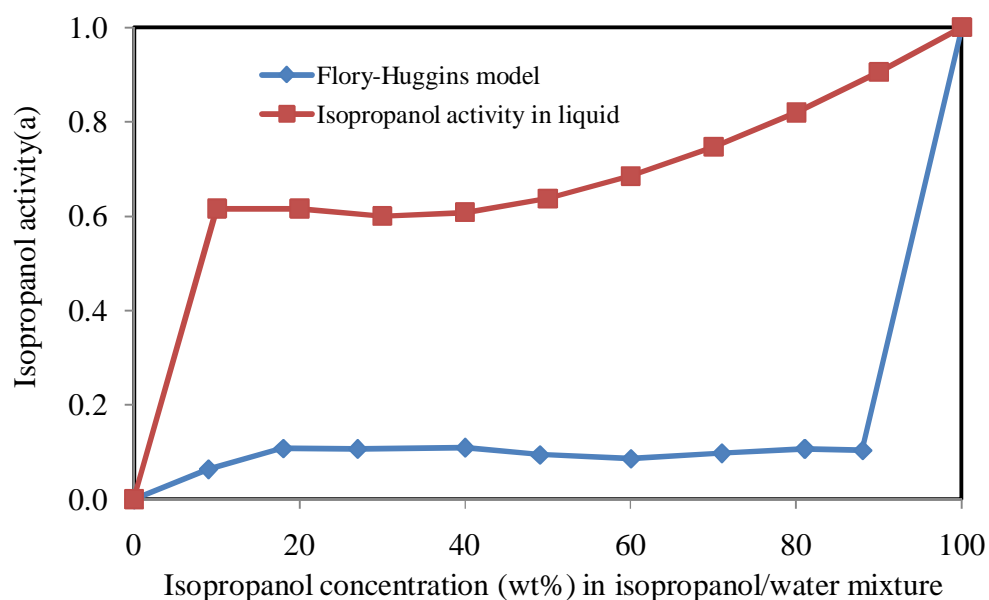


Figure 6-13 Isopropanol activity in liquid and isopropanol activity calculated using Flory-Huggins model

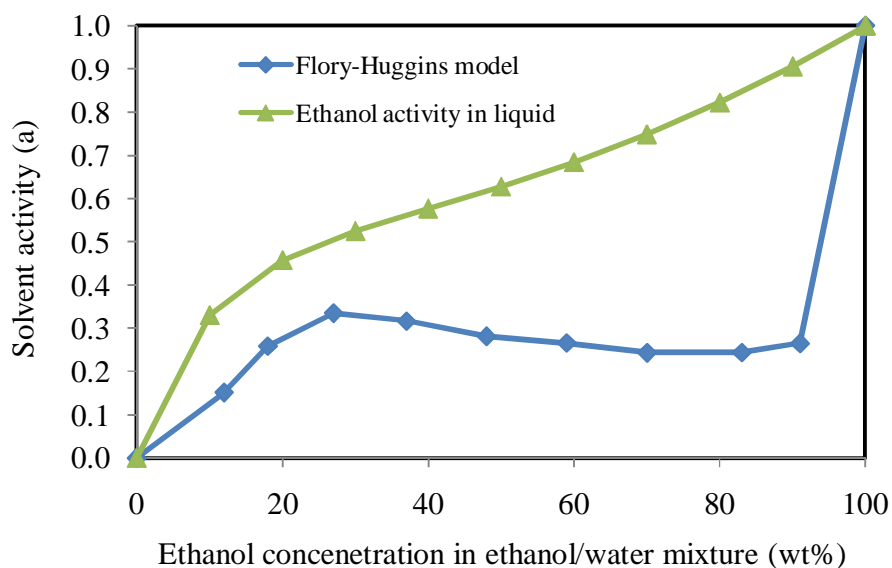


Figure 6-14 Ethanol activity in liquid and ethanol activity calculated using Flory-Huggins model

Figure 6-14 indicates that isopropanol activity in the swollen polymer determined from Flory-Huggins model is lower than observed experimentally. Similar behaviour is observed for ethanol/water as shown in Figure 6-15, however in this case the predicted activity is closer to that observed experimentally, particularly for ethanol concentrations < 30%.

The results show that a lack of quantitative prediction of alcohol activity in swollen PDMS. The Flory Huggins model does not predict the activity of alcohol in alcohol/water mixtures, hence empirical characterization will always be necessary at this stage.

6.5 PVA in alcohol/water

6.5.1 Total swelling degree

PVA samples were prepared and subjected to immersion in mixtures of alcohol/water to determine swelling degree. Figure 6-16 shows a plot of the swelling degree for PVA in ethanol/water and isopropanol/water.

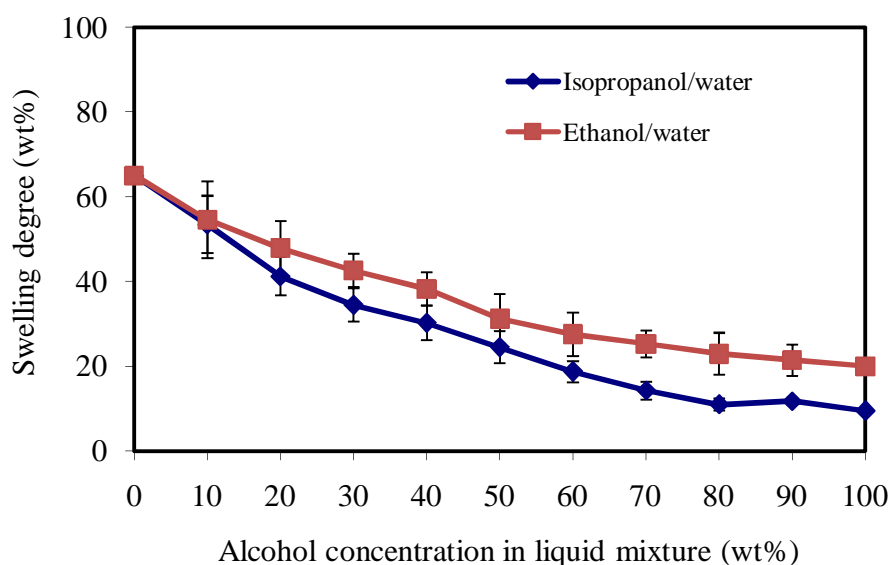


Figure 6-15 Total swelling degree at different alcohol concentrations in alcohol/water mixtures

It is apparent that the alcohol/water swells PVA throughout the entire range of mixture composition, and that swelling degree decreases with increasing alcohol concentration. This behaviour is expected because PVA polymers are hydrophilic, and so water is likely to be preferentially absorbed over alcohol. This is consistent with the swelling degree in pure solvents. From Figure 5-3, the swelling degree of PVA in ethanol and isopropanol is 20% and 9% respectively, compared with 65% for water. The same data can be used to

show swollen PVA compositions at equilibrium; these data are shown in Figure 6-17 and 6-18.

6.5.2 Change in composition due to swelling

Table 6.6 Initial concentration, the equilibrium ethanol and isopropanol concentration in swollen PVA

Alcohol concentration (wt%)	Ethanol concentration in swollen PVA (wt%)	Isopropanol concentration in swollen PVA (wt%)
10	8.2	4.3
20	14.9	9.2
30	20.7	12.0
40	24.3	15.2
50	23.2	16.0
60	21.7	13.0
70	19.9	11.1
80	19.6	9.0
90	20.8	11.0

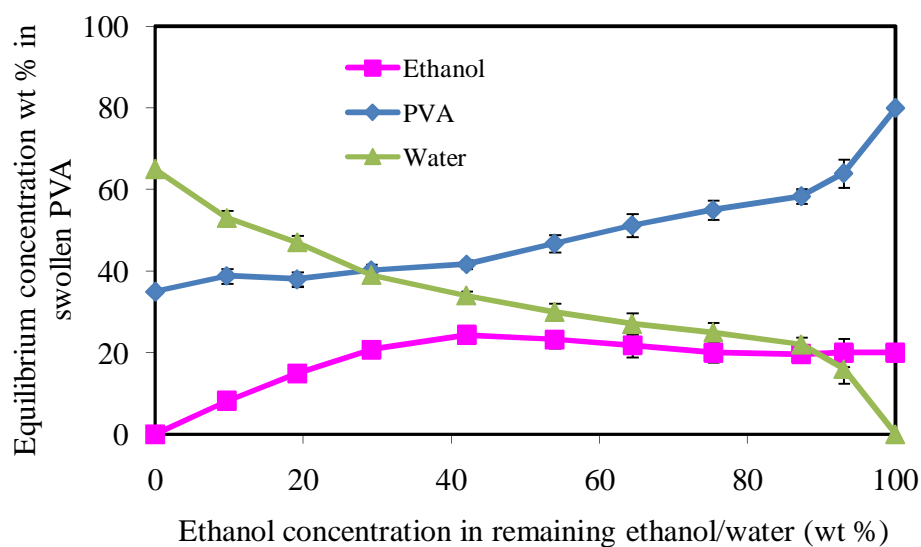


Figure 6-16 Relationship at equilibrium between ethanol, water, and PVA concentration in swollen polymer

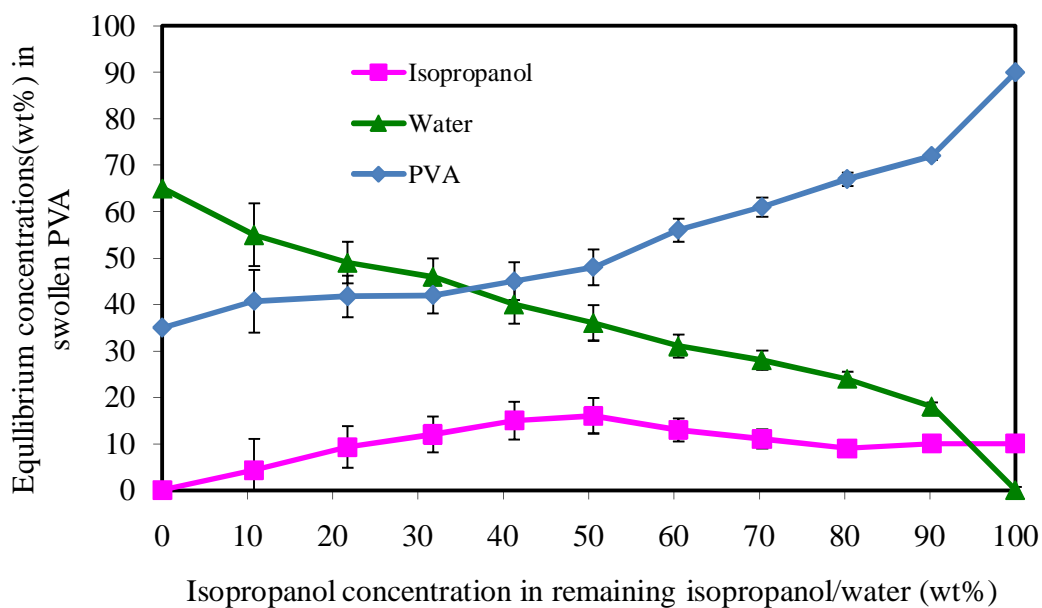


Figure 6-17 Relationship between equilibrium isopropanol, water and PVA concentrations in swollen polymer

Figure 6-17 and 6-18 show very similar trends. As the alcohol concentration increases the water concentration decreases steadily across the entire concentration range. The alcohol concentration within the polymer reaches a peak around 40-50% alcohol, whereas the extent of PVA increases steadily with increasing alcohol concentration.

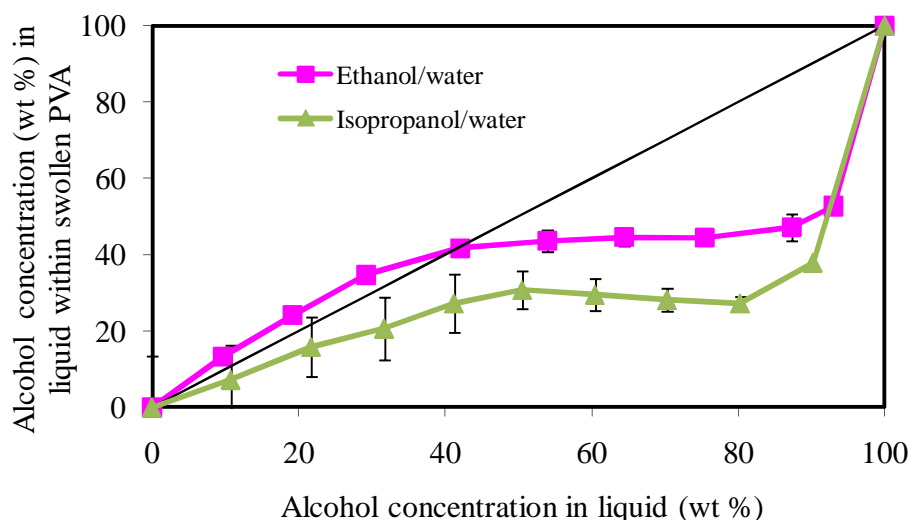


Figure 6-18 Alcohol concentrations in the liquid inside swollen PVA versus alcohol concentration in the liquid phase. The straight line ($y=x$) represents a selectivity of zero

Figure 6-19 shows alcohol composition in the liquid within the swollen polymer plotted against the equilibrium concentration in the liquid phase. The ethanol concentration in liquid within PVA is higher than that of isopropanol indicating a greater affinity of PVA to ethanol than isopropanol. PVA demonstrates a change in ethanol selectivity based on ethanol concentration, as PVA is ethanol selective from 0-42% and water selective at higher ethanol concentrations. However, PVA is water selective through the entire range of isopropanol/water concentrations. This could be attributed to competing effects of polarity and molecular size, which determine the sorption behaviour of alcohol and water. However in this case it is not possible to de-couple the two effects and hence it is difficult

to infer if any of the two mechanisms are more dominant. However, at low ethanol concentration it is apparent that ethanol is selectively absorbed, despite the ethanol molecules being larger than those of water.

6.5.3 Sorption coefficient (K) of PVA in alcohol/water

A comparison between sorption coefficient behaviour in ethanol/water and isopropanol/water is shown in Figure 6-20

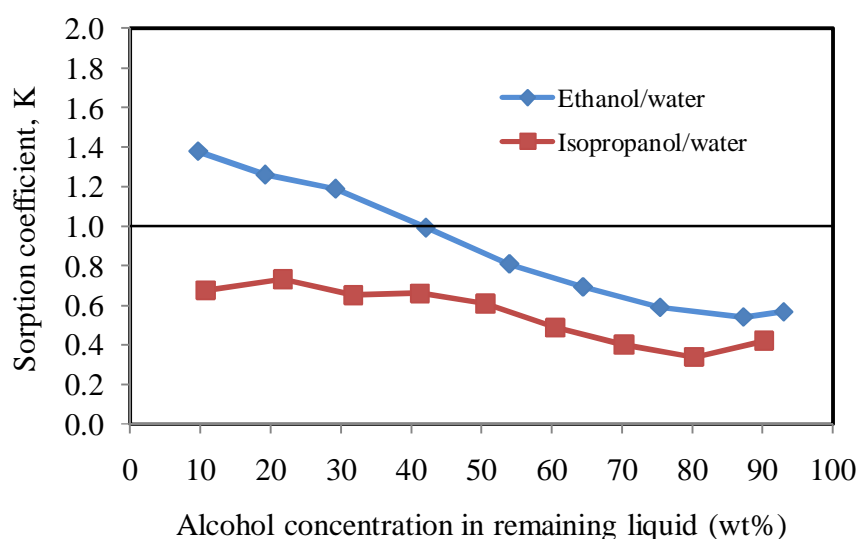


Figure 6-19 Relationship between alcohol sorption coefficient and alcohol concentration

The results show that sorption of alcohol into PVA from aqueous mixture is highly dependent on the alcohol concentration. The results show that the sorption coefficient for ethanol is higher than that for isopropanol at all concentrations investigated. The higher sorption coefficient for ethanol indicates that the affinity of PVA to ethanol is higher than that of isopropanol, and this is consistent with the swelling degree in pure solvents. PVA shows an ethanol selective region in which the sorption coefficient values are above 1, which occurs at ethanol concentrations from 0 to 42.2%. This result indicates that PVA

could be used as a candidate membrane material for ethanol separation especially, at low concentration. In this case ethanol will be selectively permeated from water, but only at low concentration. In the case of isopropanol/water, PVA will selectively permeate water across the entire concentration range and may be a good material to dehydrate isopropanol.

6.5.4 Application of Flory-Huggins theory to ternary system

The determination of ethanol/water interaction parameters (χ_{SIS2}) was performed as explained in Section 6.2.4.1. The results are shown in Table 6.5. A comparison between alcohol activity and predicted activity calculated by Flory-Huggins model ethanol/water and isopropanol/water are presented in Figures 6-21 and 6-22 respectively.

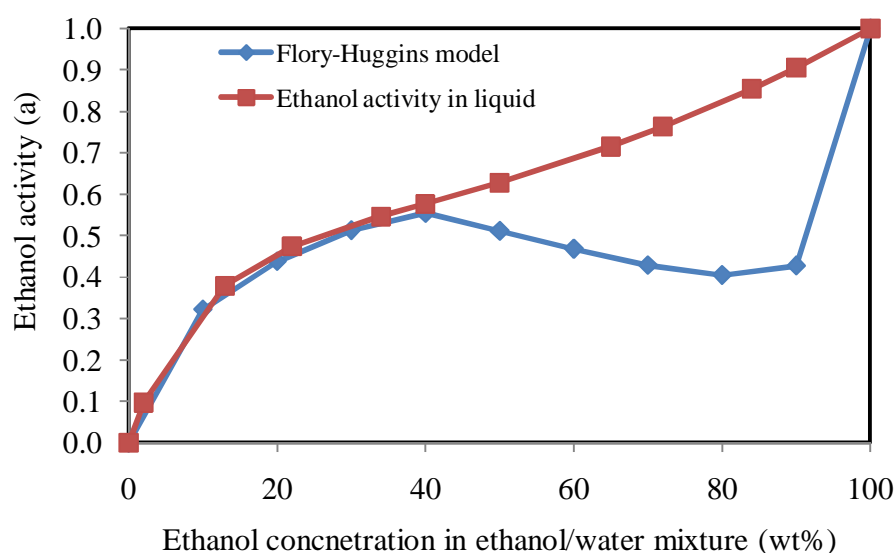


Figure 6-20 Relationship between Flory-Huggins model and experimental ethanol activity

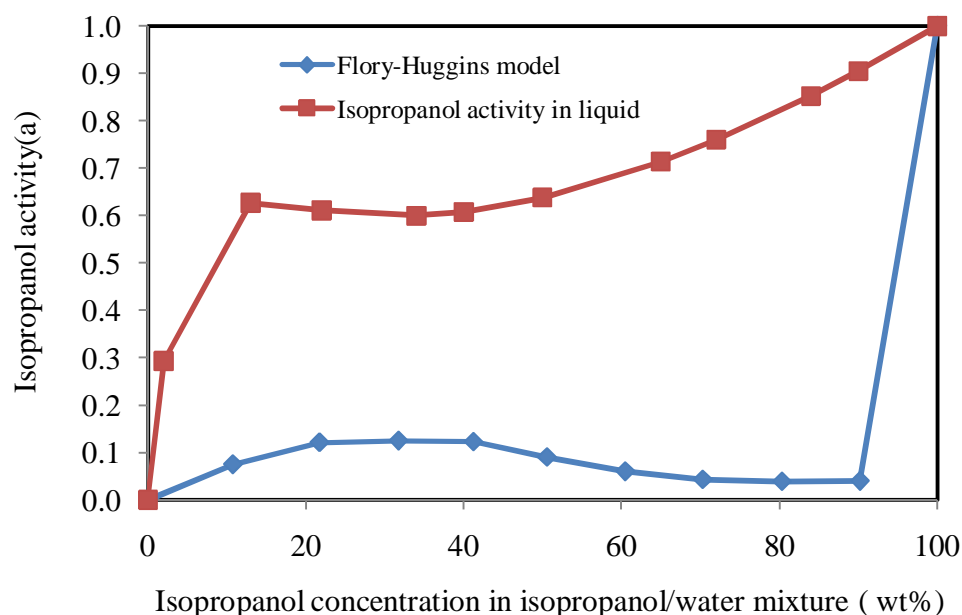


Figure 6-21 Relationship between Flory-Huggins model and isopropanol activity

The ethanol activity in swollen PVA from the Flory-Huggins model is similar to the actual ethanol activity in the concentration range between 0 to 40%. Very good agreement between theory and experiments is obtained in this region. At higher concentration there is a significant deviation between the experimental data and the Flory-Huggins model.

Figure 6-22 shows that there is no such agreement with isopropanol water, where the model and experimental data are significantly different across the entire concentration range. The results in Figure 6-22 imply that the Flory-Huggins model is not able to accurately predict the isopropanol activity.

6.6 Comparison between sorption coefficient in PDMS and PVA

6.6.1 Ethanol/water system

A comparison between ethanol sorption coefficient for PVA and PDMS is presented in Figure 6-23.

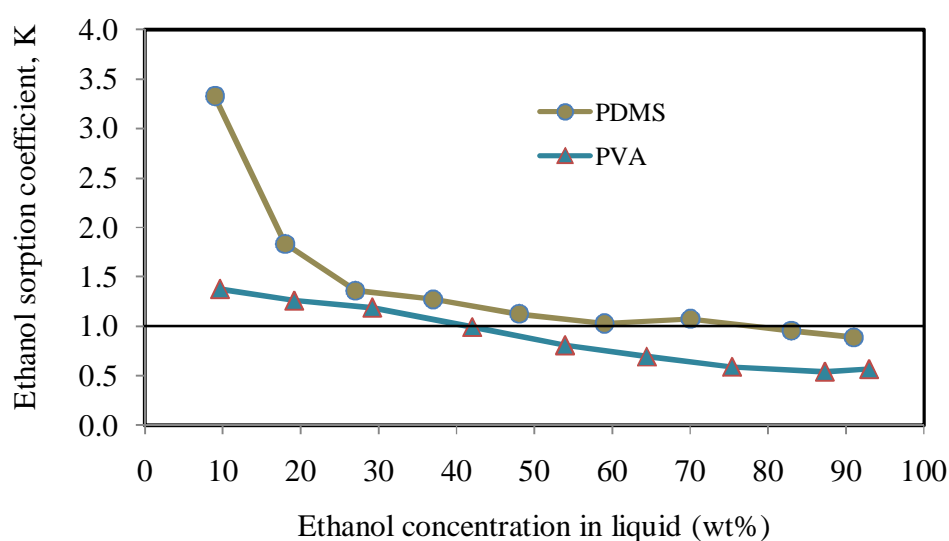


Figure 6-22 Comparison between PDMS and PVA ethanol sorption coefficient in ethanol/water mixtures

The results show that sorption coefficient for ethanol is higher in PDMS than in PVA at all ethanol concentrations. Ethanol is selectively absorbed in both polymers up to 42% ethanol. From 42 to 73% PDMS is ethanol selective and PVA is water selective, where above 73% ethanol, both materials are water selective.

The results show that for PDMS the maximum sorption coefficient is 3.3, corresponding with 1.3 for ethanol. This result indicates that the sorption selectivity of PDMS is 2.5 times higher than PVA at low concentrations. At ethanol concentrations above 80% PVA is water selective, whilst PDMS does not indicate any appreciable ethanol selectivity. The results

suggest that PVA could be used to make water-selective membranes utilised for ethanol dehydration at ethanol concentrations $> 40\%$. PDMS is more suitable when the concentration $< 40\%$, particularly at lower concentrations.

The % changes in sorption coefficient due to the increase in ethanol concentration are shown in Table 6.7, which indicates that sorption coefficient differs based on the polymer material. With increasing ethanol concentration from 10 to 90%, the corresponding change in sorption coefficient ranges from 275 to 132% for PDMS and PVA.

Table 6.7 The change in sorption coefficient due to increasing ethanol concentration

Polymer/alcohols/water systems	% change in sorption coefficient from 10- 90 wt%
PDMS /ethanol/water	275
PVA / ethanol/water	132

6.6.2 Isopropanol/water system

A comparison between isopropanol sorption coefficient in PVA and PDMS is presented in Figure 6-24.

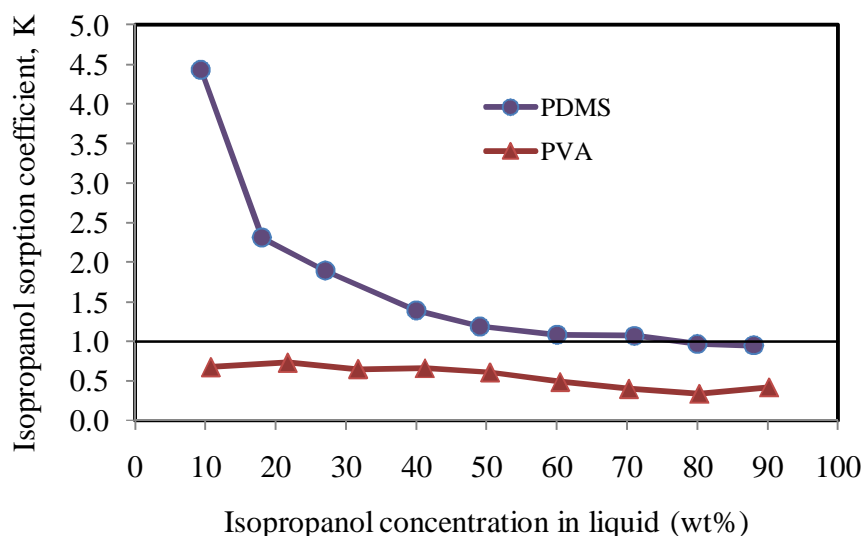


Figure 6-23 Comparison between PDMS and PVA isopropanol sorption coefficient in isopropanol/water mixtures

Over the concentration range studied the sorption coefficient values range from 4.4 to 0.9 in PDMS and from 0.67 to 0.42 in PVA. The results illustrate that isopropanol selectively in PDMS is higher than that in PVA, as PDMS preferentially absorbs isopropanol from its mixture.

The swelling degree for isopropanol in PDMS (28 wt%) is higher than that in PVA (9 wt%), indicating a much stronger affinity of PDMS to isopropanol than PVA to isopropanol. These results suggest that PDMS could be used as a membrane for isopropanol/water separation at <50% isopropanol. In this case PDMS will preferentially absorb isopropanol and reject water. PVA could also be used for isopropanol/water separation, as it preferentially absorbs water across the entire concentration range.

The % changes in sorption coefficient due to the increase in isopropanol concentration are shown in Table 6.8, which indicates that sorption coefficient differs based on the polymer

material. With increasing isopropanol concentration from 10 to 90%, the corresponding change in sorption coefficient ranges from 365 to 59% for PDMS and PVA.

Table 6.8 the change in sorption coefficient due to increasing isopropanol concentration

Polymer/alcohols/water systems	% change in sorption coefficient from 10- 90 wt%
PDMS /isopropanol/water	363
PVA /isopropanol/water	59

6.7 Conclusions

The results obtained in this study conclude that the degree of swelling highly dependent on the mixture concentration and solvent type. The sorption of solvents in the polymer depends on the competing effect of polarity and molecular size. Both PDMS and PVA were found to exhibit significant degrees of selectivity to one of the solvents within the mixture. The selectivity is highly dependent upon the concentration of the mixture, and there are several cases whereby the polymer selectively switches from one solvent towards the other. This was observed with PDMS in ethanol/n-hexane, ethanol/n-heptane, ethanol/water, and isopropanol/water. It also observed with PVA in ethanol/water. However PVA was found to be water-selective across the full isopropanol concentration range. The sorption coefficient data indicates that PDMS or PVA are suitable membrane materials for alcohol/water separation.

The predictability of the sorption coefficient was assessed using the Flory-Huggins model. There is a general agreement between theory and experimental data for PVA ethanol, and water mixtures when ethanol concentration < 40%. However there was limited agreement

> 40%, and no agreement for isopropanol/water/PVA or for any system with PDMS. This indicates that Flory-Huggins model is of very limited use in predicting polymer swelling with solvent mixture. This limitation could be due to the assumption of constant polymer/solvent interaction parameters, and it is possible that a more accurate predictive technique could be developed if this factor were to be taken into account. It is clear that the selectivity of PDMS and PVA is highly non linear and unpredictable. At this stage it is necessary to carry out experiments to assess the suitability of a polymer for use as a membrane, rather than use predictive techniques.

Chapter 7 EFFECT OF POLYMER CROSSLINKING

CONTENT ON SELECTIVITY

7.1 Introduction

Permeability and selectivity depend on the microstructure of the polymer network, which in turn is influenced by the conditions of its preparation, including crosslinking content. Swelling of PDMS and PVA in alcohol/water mixtures was performed for different crosslinking contents, and the results evaluated. Alcohol sorption in the polymer from the alcohol/water mixture was evaluated using the sorption coefficient to quantify the selectivity due to sorption.

7.2 Comparison with literature

In order to validate the technique used in this study, the experimental results were compared to those reported by Stafie *et al.* [234]. They prepared PDMS with different crosslinker content by changing the ratio of RTV615A to RTV615B, 10/0.7, 10/1 and 10/2, corresponding to a crosslinker content of 6.5, 9.1, and 16.7% respectively. Their data were compared with the swelling data obtained in this work and the results shown in Figure 7-1

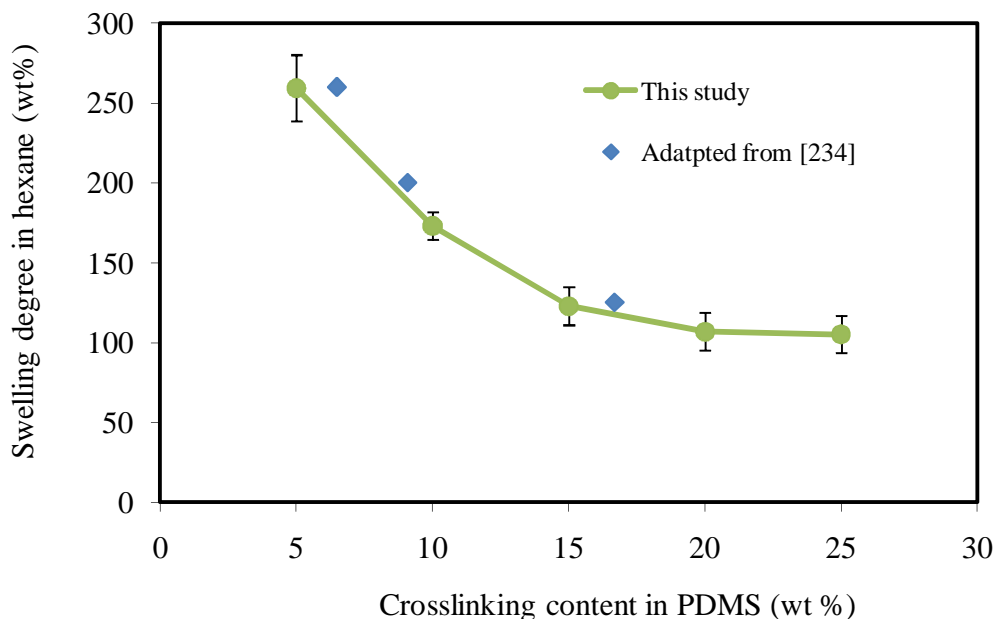


Figure 7-1 Relationship between swelling degree of PDMS in hexane at different crosslinking content, and comparison with literature.

The results indicate that swelling degree decreases with increasing crosslinking content for both trends. Increasing crosslinking content leads a more rigid polymer network structure, which makes the polymer matrix more rigid. This in turn results in less free volume, which reduces the amount of absorbed liquid in the polymer. The two studies show a good quantitative agreement. The same experimental technique was used to investigate the effect of crosslinking content on the swelling degree in different solvents.

7.3. Alcohol/water sorption in PDMS

7.3.1 Effect of crosslinking content on swelling degree

The swelling of PDMS in ethanol, isopropanol, 30% ethanol in water and 30% isopropanol in water mixtures was determined. The swelling degree at equilibrium was expressed as a

CHAPTER SEVEN EFFECT OF POLYMER CROSSLINKING CONTENT ON SELECTIVITY

percentage according to Equation 3.2. The influence of crosslinking content on swelling in ethanol, isopropanol, 30% ethanol in water and 30% isopropanol in water mixtures is presented in Figures 7-2 and 7-3.

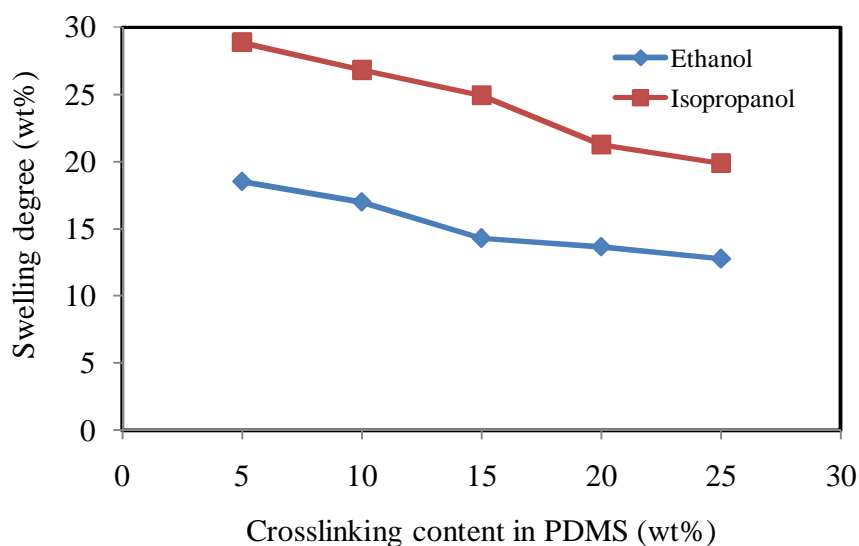


Figure 7-2 Swelling degree in ethanol and isopropanol

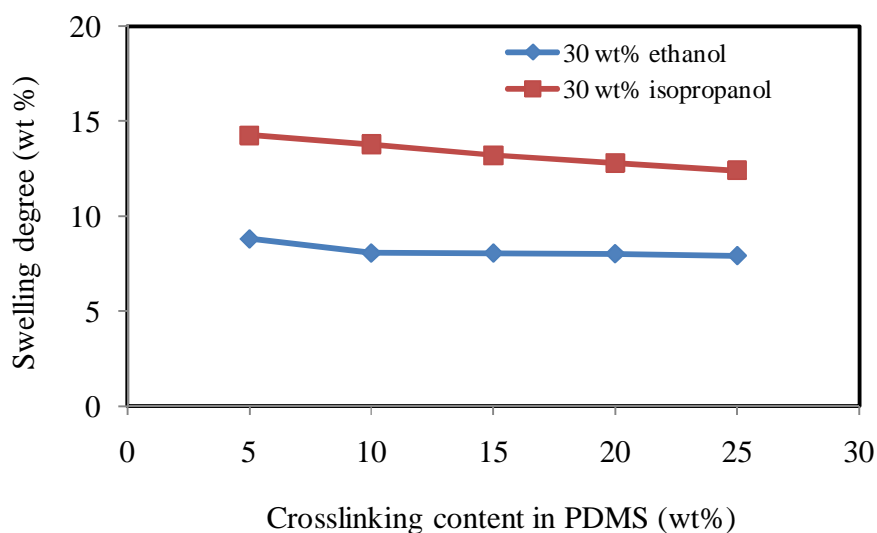


Figure 7-3 Swelling degree in alcohol/water mixtures

The results show that swelling degree is inversely proportional to the cross linking content for all trends. In Figure 7-2, the swelling degree in ethanol and isopropanol decreases from 18 to 12.5% and 28 to 19.8% respectively. In Figure 7-3, the swelling degree in 30% ethanol and 30% isopropanol decreases from 8.8 to 7.9% and 14.2 to 12.4% respectively. This behaviour is expected because the PDMS network becomes more rigid, resulting in less free volume, and reduced alcohol and water sorption into the polymer matrix. The addition of crosslinker also reduces the hydrophobicity of PDMS, which influences the sorption of alcohol (ethanol or isopropanol from its mixtures) into the polymer.

The results show that the swelling degree for isopropanol is higher than that of ethanol for pure and aqueous mixtures at all crosslinking contents. This is consistent with the swelling degree in pure solvents as swelling degree in isopropanol is higher than that of ethanol. The swelling degree for alcohols is approximately two times higher than the swelling degree for the alcohol/water mixture, indicating greater affinity of polymer to alcohol than the mixture. The results show a larger change in swelling degree for alcohols and minor change for the alcohol/water mixture with crosslinking. The overall degrees of swelling reduce with increasing PDMS crosslinking content and water concentrations.

7.3.2 Effect of crosslinking content on alcohol sorption

The swelling equilibrium studies were also extended to investigate alcohol concentration within the liquid inside the swollen polymer. PDMS samples of varying crosslinking content were immersed in flasks containing 30% alcohols in water. Alcohols concentrations in the swollen polymers was calculated based on mass balance as described in Section 3.5 and the composition of the swollen polymer in ethanol/water and isopropanol/water are shown in Tables 7.1 and 7.2 respectively.

CHAPTER SEVEN EFFECT OF POLYMER CROSSLINKING CONTENT ON SELECTIVITY

Table 7.1 Ethanol, water and PDMS concentrations in the swollen polymer

PDMS crosslinking content (wt%)	Ethanol concentration in swollen polymer (wt%)	Water concentration in swollen PDMS (wt%)	PDMS concentration in swollen polymer (wt%)
5	11.2	16.6	72.2
10	11.6	15.3	73.0
15	12.0	14.0	74.0
20	12.4	12.4	75.2
25	13.0	12.5	74.5

Table 7.2. Isopropanol, water and PDMS concentrations in the swollen polymer

PDMS crosslinking content (wt%)	Isopropanol concentration in swollen polymer (wt%)	Water concentration in swollen PDMS (wt%)	PDMS concentration in swollen polymer (wt%)
5	14.2	13.7	72.0
10	14.8	13.2	72.1
15	15.3	12.4	72.3
20	15.8	11.3	72.9
25	16.0	10.6	73.4

The results in Tables 7.1 and 7.2 show the composition of the swollen PDMS at different crosslinking contents. The contribution of PDMS in the swollen polymer can be excluded and the results interpreted in terms of the alcohols/water ratio. Alcohol sorption from

CHAPTER SEVEN EFFECT OF POLYMER CROSSLINKING CONTENT ON SELECTIVITY

aqueous alcohol mixtures within the liquid in the swollen polymer are presented in Figure 7-4.

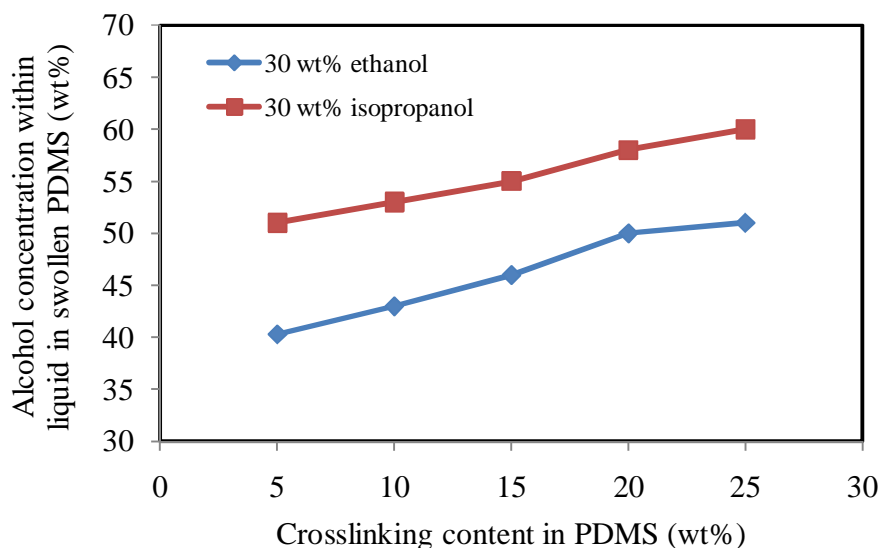


Figure 7-4 Effect of crosslinking content on alcohol sorption in swollen PDMS

Figure 7-4 shows that the weight fraction of ethanol within the liquid absorbed in the polymer increases from 40.3 to 51.0% as the crosslinking content increases from 5 to 25%. Over the same range of crosslinking content the corresponding isopropanol concentration increases from 51 to 60%. The results show that isopropanol concentration within the liquid is higher than that of ethanol at all crosslinking contents. Both trends indicate that the alcohol concentration increases upon increasing the crosslinking content. The results illustrate that alcohol concentration within the liquid in the swollen polymer is higher than the initial alcohol concentration, and indicates an alcohol-rich PDMS polymer, which is alcohol selective.

CHAPTER SEVEN EFFECT OF POLYMER CROSSLINKING CONTENT ON SELECTIVITY

Summarising the above results it can be seen that PDMS, at all crosslinking contents investigated is selective towards alcohol. This result points to the potential ability to alter the selectivity of PDMS for ethanol and isopropanol extraction in a separation process for aqueous solutions. For extraction of ethanol and isopropanol from water, the required selectivity could be adjusted by changing the crosslinking content of the prepared polymer.

7.3.3 Alcohol sorption coefficient

Composition studies were also extended to investigate the alcohol sorption coefficient at different crosslinking contents. The sorption coefficients of ethanol in ethanol/water mixture and isopropanol in isopropanol/water mixtures are shown in Figure 7-5

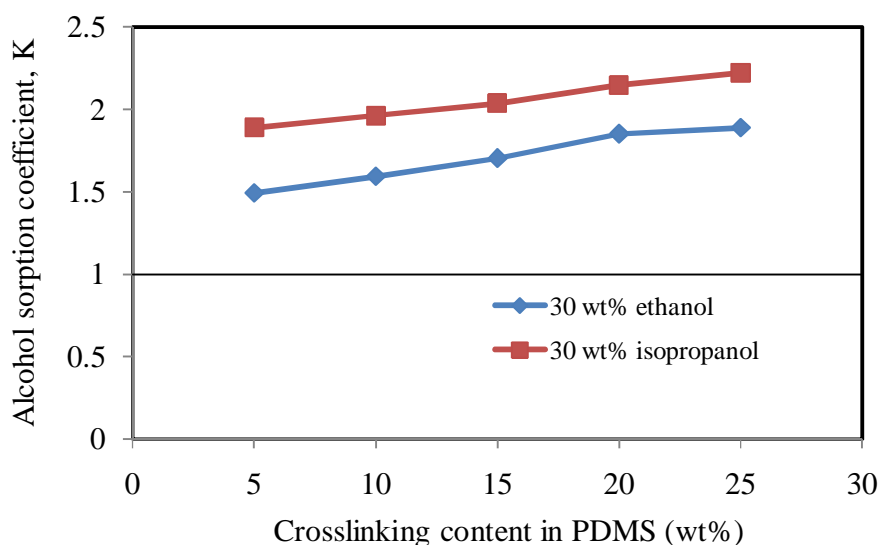


Figure 7-5 Relation between crosslinking content and alcohol sorption coefficient for ethanol/water and isopropanol/water mixtures

The results show that the sorption coefficient for isopropanol is higher than that of ethanol at all crosslinking contents. This is expected because the swelling degree in isopropanol is

higher than that in ethanol. Both trends indicate that sorption coefficient increases with increasing crosslinking content. Over the 5 to 25% range, sorption coefficients for ethanol rise from 1.49 to 1.88, and for isopropanol from 1.89 to 2.22.

The results demonstrate that sorption coefficients are a function of polymer crosslinking. Nguyen *et al.* [205, 249] investigated the swelling and sorption properties of PDMS materials crosslinked under different conditions. They found an increase in ethyl acetate sorption in the swollen polymer due to increase PDMS crosslinking content, and attributed the difference in sorption of ethyl acetate from water to the addition of more cross-linker, which in their view led to reduced membrane free volume, and change the hydrophobicity/hydrophilicity of the polymer.

7.4. Alcohol/water sorption in PVA

7.4.1 Effect of crosslinking content on total swelling degree

PVA samples of varying crosslinking content were immersed in flasks containing water, 30% ethanol in water and 30% isopropanol in water. The swelling degree is shown in Figure 7-6.

CHAPTER SEVEN EFFECT OF POLYMER CROSSLINKING CONTENT ON SELECTIVITY

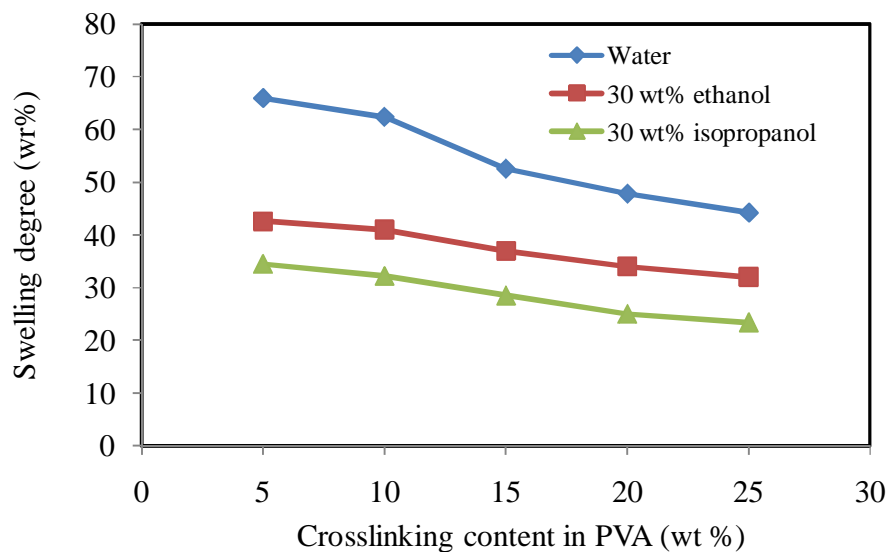


Figure 7-6 Swelling in water and alcohol/water mixtures at different crosslinking contents.

The results show that the swelling degree in 30% alcohol is lower than that of water at all crosslinking content. As the crosslinking content increases from 5 to 25%, the swelling degree decreases for both water and alcohol/water mixtures. For water, the highest swelling degree is 65% at a crosslinking content of 5%, and the lowest swelling degree is 44% at a crosslinking content of 25%. As crosslinking content is increased from 5 to 25%, the polymer swelling degree decreases from 42.6 to 32% for 30% ethanol and from 34 to 23.4 for 30% isopropanol.

The results show that swelling degree is inversely proportional to cross linking content for all systems studied. The data indicates that an increase in crosslinking content leads to the polymer structure becoming more rigid. There is a reduced chain length between cross-links as a result of increased crosslinker content, which leads a stronger elastic resistance to swelling. Moreover, the addition of more crosslinker to the polymer network causes the free volume in the polymer to diminish, which reduces the ability of the polymer to absorb

CHAPTER SEVEN EFFECT OF POLYMER CROSSLINKING CONTENT ON SELECTIVITY

water and alcohol from the mixture. The amount of crosslinker can affect the polymer hydrophilicity, which in turn can influence the sorption of each component in the polymer. The combined effects of a reduction in free volume and changes to the surface properties of the polymer mean that increasing polymer crosslinking content decreases the degree of polymer swelling for both water and aqueous alcohol solutions.

7.4.2 Effect of crosslinking content on alcohol sorption

The swelling equilibrium studies were also developed to explore ethanol concentration within the liquid inside the swollen polymer at different crosslinking content. PVA samples of varying crosslinking content were immersed in flasks containing 30% ethanol and 30% isopropanol in water. Experiments were carried out as shown in Section 3.5. The results are shown in Tables 7.3 and 7.4, which shows how the equilibrium composition varies as the PVA crosslinking content is altered.

Table 7.3. Crosslinking content in PVA and corresponding ethanol, water, and PVA concentrations in the swollen polymer.

PVA crosslinking content (wt%)	Ethanol concentration in swollen polymer	Water concentration in swollen PVA	PVA concentration in swollen polymer
5	20.7	38.9	40.3
10	20.0	38.8	41.2
15	19.2	38.9	41.8
20	18.0	38.9	43.0
25	17.3	38.7	43.2

CHAPTER SEVEN EFFECT OF POLYMER CROSSLINKING CONTENT ON SELECTIVITY

Table 7.4. Crosslinking content in PVA and corresponding isopropanol, water, and PVA concentrations in the swollen polymer.

PVA crosslinking content	Isopropanol concentration in swollen polymer	Water concentration in swollen polymer	PVA concentration in swollen polymer
5	12.0	46.2	41.7
10	11.0	46.8	42.1
15	9.7	47.3	42.9
20	7.9	48.5	43.5
25	7.1	49.2	43.7

The results in Tables 7.3 and 7.4 show the composition of the swollen PVA at different crosslinking contents. By excluding the contribution of PVA, the results can be interpreted in terms of alcohol/water ratio, which is presented in Figure 7-7.

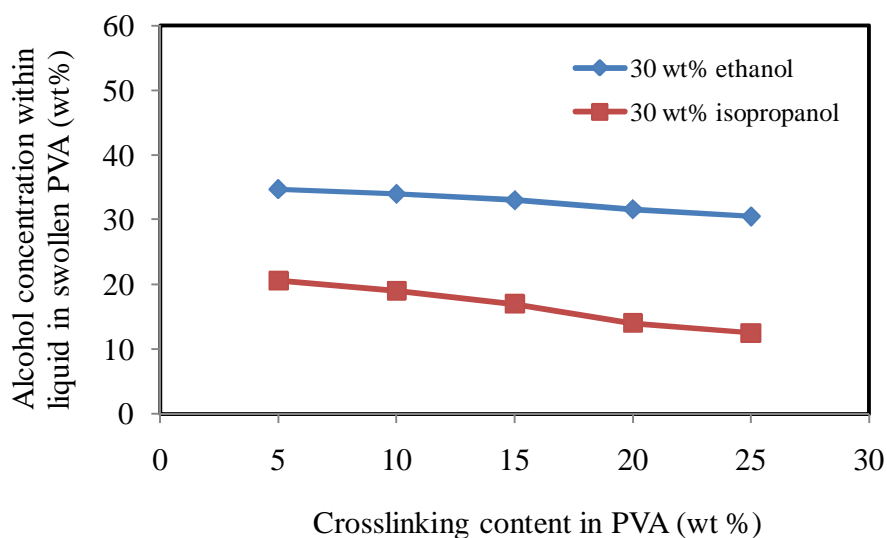


Figure 7-7 Effect of PVA crosslinking content on concentration within liquid in swollen PVA

CHAPTER SEVEN EFFECT OF POLYMER CROSSLINKING CONTENT ON SELECTIVITY

Figure 7-7 shows that as PVA crosslinking content increases from 5 to 25%, the concentration within swollen polymer decreases from 34.7 to 30.5 % for ethanol, and from 20.6 to 12.5% for isopropanol. The results show that the ethanol concentration is higher than that of isopropanol at all crosslinking contents. Moreover, both trends indicate that alcohol concentrations decrease with increasing crosslinking content.

The sorption of alcohols in PVA appears to depend on competing effects of molecular size and polarity. If solvent polarity is not considered, molecular size can potentially explain the sorption observations. The molecular size can be qualitatively classified as water < ethanol < isopropanol, and sorption decreases with increasing molecular size. As the crosslinking content is increased, the free volume decreases therefore these components with the lowest molecular size can occupy the space within the polymer matrix. If there is a small volume available, the smaller the size the better the penetration. The variation of selectivity between ethanol and isopropanol may be attributed to the difference molecular size, as there is a difference in number of carbon atoms. It is clear that with an increase in the number of carbon atoms of the absorbed species, PVA selectivity towards alcohols decrease.

Another observation is that the study uses at 30% alcohol, and the isopropanol concentration within liquid inside the swollen polymer is always lower than this concentration, which means that the polymer is water selective. The water selectivity increases with increasing crosslinking content. However the ethanol concentration within the liquid inside swollen polymer is always higher than the feed concentration, which means that the polymer is ethanol selective, and the ethanol selectivity decrease with increasing crosslinking content.

CHAPTER SEVEN EFFECT OF POLYMER CROSSLINKING CONTENT ON SELECTIVITY

In addition, PVA absorbs water in preference to isopropanol; which is enhanced by the increased crosslinking content and leads to a water-rich PVA polymer matrix. It is hypothesized that tighter polymer network will be more retentive to isopropanol and thus prevent them from penetrating through the polymer matrix. Therefore PVA becomes more water selective in an isopropanol/water mixture.

The results show that crosslinking content affects PVA selectivity by changing either the concentration of alcohol or water within liquid in swollen polymer. In such a process, varying the crosslinking content during polymer preparation could allow the required selectivity to be achieved.

7.4.3 Alcohol sorption coefficient

The ratio of alcohol concentration in the swollen polymer to alcohol concentration in the remaining solution represents the alcohol sorption coefficient. The sorption coefficients of ethanol and isopropanol are shown in Figure 7-8 as a function of crosslinking content.

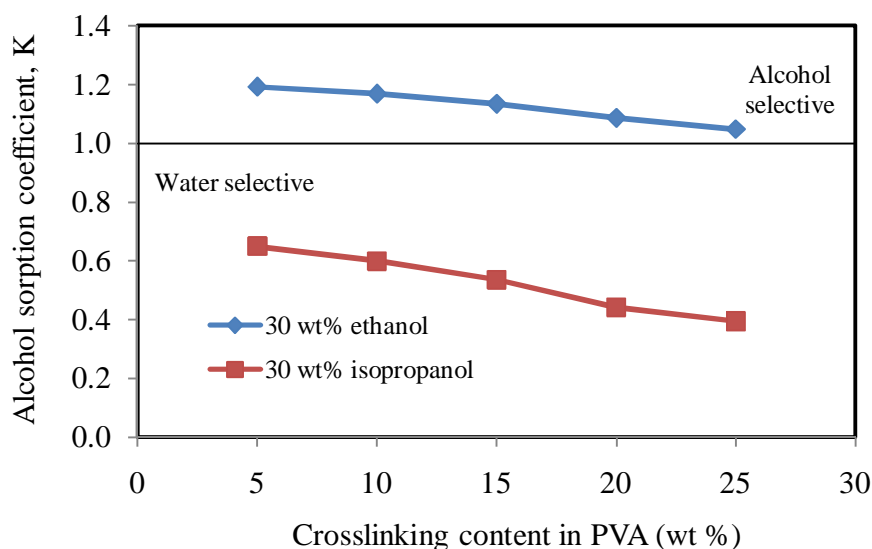


Figure 7-8 Relation between crosslinking content and alcohol sorption coefficient in ethanol/water and isopropanol/water mixtures

CHAPTER SEVEN EFFECT OF POLYMER CROSSLINKING CONTENT ON SELECTIVITY

Both trends in Figure 7-8 indicate that the alcohol sorption coefficient decreases with increasing PVA crosslinking content. The sorption coefficient for ethanol is higher than isopropanol at all crosslinking content investigated. The higher sorption coefficient for ethanol indicates that the affinity of PVA to ethanol is higher than that of isopropanol, and this is consistent with the swelling degree in pure solvents. From Figure 5-3, the swelling degree of PVA in ethanol is 20%, compared with 9% for isopropanol. This in turn is explained by the fact that the solubility parameter of ethanol is closer to the solubility parameter of PVA than that of isopropanol.

When the sorption coefficients are higher than 1, the polymer is alcohol selective. As the crosslinking content increases from 5 to 25% the sorption coefficient decreases from 1.19 to 1.04 for ethanol, whilst it decreases from 0.64 to 0.39 for isopropanol. This indicates that the polymer is ethanol selective from ethanol/water.

The behaviour shown in Figure 7-8 can be attributed to a change in alcohol concentrations as governed by the corresponding alcohol fugacities. At equilibrium, the chemical potential of alcohol at the alcohol feed side equals the chemical potential of alcohol component at the polymer side. Assuming that the molar volume of alcohol does not change between the liquid phase and swollen polymer phase, the activity of alcohol at the feed side equals that at the polymer side. From Equation 2.23, the resulting change in concentration between the feed side and polymer side is due to the change in the activity coefficient. The presence of PVA in the swollen polymer phase changes the activity coefficient of alcohol from the value exhibited by the liquid mixture, and this in turn dictates the concentration within the polymer at equilibrium. The change in the activity coefficient also appears to be dependent on the degree of crosslinking.

CHAPTER SEVEN EFFECT OF POLYMER CROSSLINKING CONTENT ON SELECTIVITY

These results demonstrate that sorption coefficient values are a function of alcohol concentration and polymer crosslinking. PVA at all crosslinking content investigated, is selective towards ethanol in ethanol/water and towards water in isopropanol/water.

Burche *et al.* [84] demonstrated that the sorption of PVA in aqueous alcohol systems depends on the feed concentration, cross-linker loading and the shape and size of the permeating species. They proposed that large molecules require a large amount of energy to penetrate the polymer matrix. Namboodiri *et al.* [92] also showed that PVA membrane performance depends on the crosslinking content. However, Lee *et al.* [95] found that the degree of PVA crosslinking influenced isopropanol permeation flux and selectivity due to crystallinity, and the number of polar side groups in PVA. They also concluded that the flux of water and isopropanol was inversely proportional to the degree of PVA crosslinking, while the selectivity of PVA for water was proportional to the crosslinking content.

7.5. Sorption coefficients of alcohols in PDMS and PVA

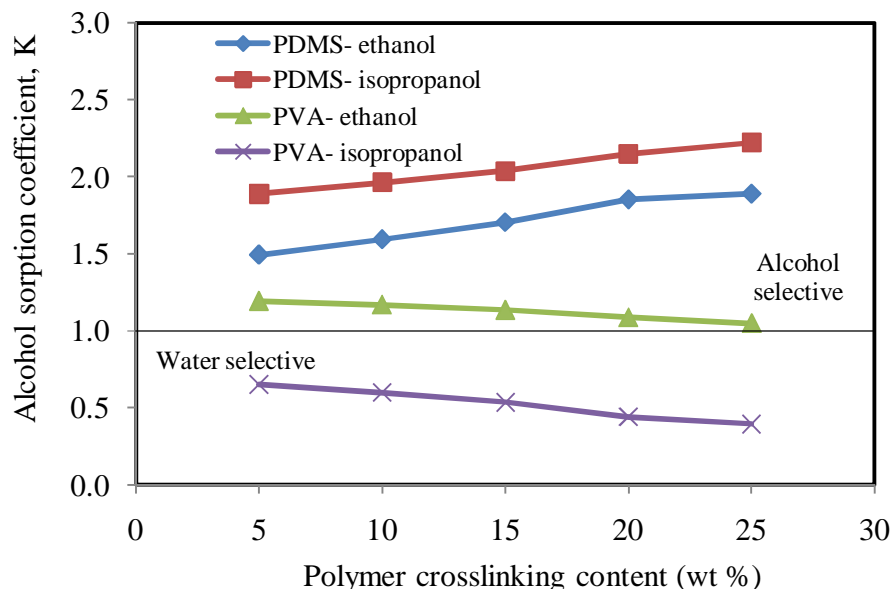


Figure 7-9 Comparison of PDMS and PVA polymers in 30% aqueous alcohol mixture for different polymer crosslinking contents

The results indicate that alcohol sorption behaviour differs based on the polymer material. When the polymer crosslinking content increases from 5 to 25%, the corresponding alcohol sorption coefficient increases for PDMS, and decreases for PVA. Selectivity can be adjusted using different crosslinking contents, and selectivity towards alcohol or water could be adjusted based on the membrane material used. PDMS could be used to extract alcohol selectively, and PVA could be used to extract ethanol and remove water from isopropanol selectively. These results demonstrate that PDMS is selective towards alcohols at all crosslinking content. However PVA, at all crosslinking content investigated, is selective towards ethanol in ethanol/water and towards water in isopropanol/water.

CHAPTER SEVEN EFFECT OF POLYMER CROSSLINKING CONTENT ON SELECTIVITY

The results demonstrate that membrane crosslinking plays an important role in aqueous solution separation. Polymer materials for dehydration should maintain a suitable crosslinking content as there is a selectivity-permeability trade off, i.e. permeability typically varies inversely with selectivity. Thus, membranes with desirable permeability often do not have a desirable selectivity. For ethanol extraction a membrane with high selectivity, such as PDMS can be used. For isopropanol dehydration PVA, which exhibits a high water selectivity, could be used.

The % changes in sorption coefficient due to the change in crosslinking content are shown in Table 7.5, which indicates that crosslinking content has only a small effect on the sorption coefficient compared to the change in sorption coefficient due to a change in alcohol concentration from 10 to 90%. The results indicate that alcohol sorption behaviour differs based on the polymer material as the % changes in sorption coefficient is highest for PVA / isopropanol/water and the lowest is for PVA / ethanol/water.

Table 7.5 Change in sorption coefficient due to increasing crosslinking content

Polymer/alcohol/water systems	% change in sorption coefficient from 5-25 wt%	% change in sorption coefficient from 10- 90 wt%
PDMS /ethanol/water	20	275
PDMS /isopropanol/water	15	363
PVA / ethanol/water	14	132
PVA / isopropanol/water	64	59

7.6 Conclusions

Increasing polymer crosslinking content decreases the degree of polymer swelling for PDMS and PVA in pure alcohol and aqueous alcohol solutions. The alcohol sorption is influenced by the addition of cross-linker to the polymer matrix, which reduces the polymer free volume through which molecules can be absorbed. The alcohol concentration in the liquid within swollen polymer also depends on the hydrophilicity/hydrophobicity of the polymer. With increasing crosslinking content, the ratio of hydrophilic to hydrophobic affiliation in polymers changes; the degree to which a polymer can swell is reduced, in turn reducing polymer alcohol sorption. The selectivity can be tailored by changing crosslinking content. However it is shown that the selectivity is more dependent upon the mixture concentration than the degree of crosslinking.

The degree of crosslinking affects the sorption coefficient, the higher the level of crosslinking between the polymer chains, the more alcohol-selective PDMS polymers become, and the less alcohol-selective PVA polymers become. However, PDMS presented a higher isopropanol sorption coefficient than that of ethanol, and PVA had an ethanol sorption coefficient that was higher than that for isopropanol.

Chapter 8 EFFECT OF PRESSURE ON POLYMER SELECTIVITY

8.1 Introduction

This chapter aims to assess membrane selectivity during the filtration process, which requires experiments to be conducted under a variable pressure environment. The difficulties of determining membrane selectivity due to the change in membrane structure, either by swelling induced by solvent or compaction induced by an applied pressure during filtration, remain unresolved. An experimental system was designed to allow both the total swelling degree and the alcohol compositions within the polymer to be measured at pressures up to 20 bar. A diagram of the apparatus is presented in Section 3.6.

8.2 Effect of pressure on PDMS swelling in different solvents

In order to study the effect of pressure on the swelling degree the experimental system was compared with the apparatus used by Tarleton *et al.* [246], a method based on the difference between swollen membrane thickness and dry membrane thickness. They developed an apparatus for in situ determination of membrane swelling in a range of alkane, aromatic, and alcohol solvents, which measured the expanded thickness of a membrane in one dimension.

For the purpose of comparison, the membrane in Tarleton *et al.* [246] comprised 10 μm PDMS layer on an area of $2\text{cm} \times 2\text{cm}$. Their membrane thickness expansion and compression values were used to calculate the swelling ratio; expressed by Equation 8.1 and compared to swelling degree calculated in this work.

$$SR \% = \left(\frac{l_{fp}}{l_{ip}} \right) \times 100 \quad (8.1)$$

Where l_{fp} is the final swollen thickness and l_{ip} is the initial thickness of dry polymer.

Polymer samples were prepared for swelling measurements according to the method detailed in Section 3.6. A piece of pre-weighed polymer was immersed in a flask containing solvent of known weight, which was present in large excess compared to the amount of polymer. The polymer was allowed to swell until it reached equilibrium, and was then transferred with its liquid to the pressure cell, where a certain pressure was applied to the polymer and liquid. Swelling experiments in different solvents were performed under pressure and those results in heptane and xylene were compared with Tarleton *et al.* [246] as shown in Figure 8-1.

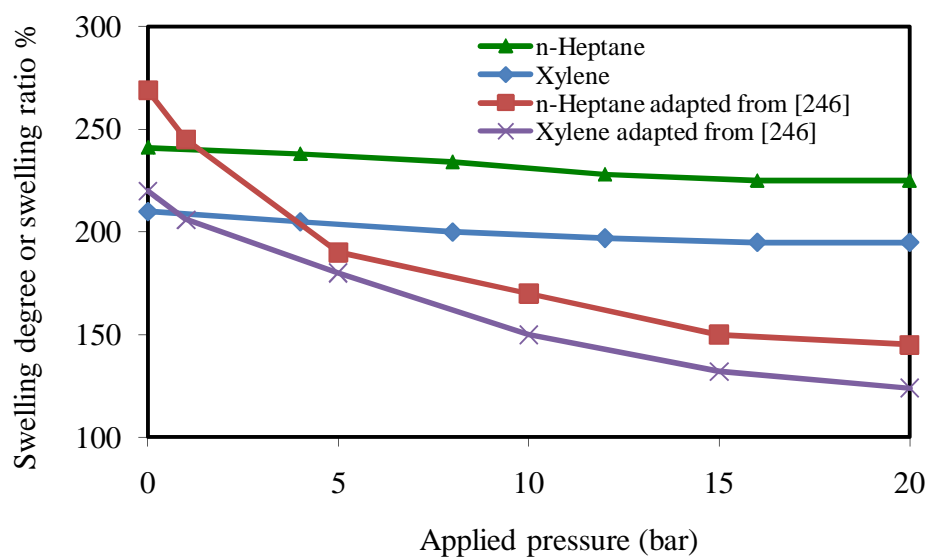


Figure 8-1 Comparison of swelling data with

The results indicate that pressure causes a reduction in the total swelling degree for both solvents and for both experimental systems. Increasing pressure from 0 to 20 bar leads to a

corresponding decrease in swelling from 241% and 208% to 225% and 195% for n-heptane and xylene respectively. Over the same pressure range, the corresponding swelling degree obtained from Tarleton *et al.* [246] for heptane and xylene decrease from 269 and 220 volume% to 145 and 124 volume % respectively. There is clearly a difference between the results obtained in this study and those of Tarleton *et al.* [246]. It is thought that this difference may be attributed to some or all of the following:

1. The artefact of the measurement method employed in both studies. In this study the whole polymer was under pressure, resulting in a force applied in three dimensions. Tarleton *et al.* [246] simulated the effect of pressure by applying mechanical forces in one dimension only, using a cantilever bar. They assumed that the expanded/compressed membrane thickness represents polymer swelling due to the one-dimensional force. It is possible that swollen polymer could expand in the other two dimensions to counteract the vertical force. If this was the case then the membrane could appear to be more compressible using the technique employed by Tarleton *et al.* [246].
2. The difference in crosslinking methods employed in both studies. The crosslinking method used in this study is a thermal crosslinking method (as explained detailed in Chapter 3), whereas Tarleton *et al.* [246] used membranes manufactured using a radiation crosslinking technique. The nature and properties of the polymers used in each case could be very different based on both the degree of crosslinking and the crosslinking method.
3. The difference in PDMS materials employed in both studies. The PDMS used in this study was manufactured from RTV615A and RTV615B, however the material used to make the membrane studied by Tarleton *et al.* [246] was not specified. The nature and properties of the PDMS polymers studied could have been different in each case based on the constituent and chemical composition of the materials used for manufacture.

4. The presences of polyacrylonitrile (PAN) support material. The study reported by Tarleton *et al.* [246] used a membrane material rather than a polymer block as used in this work. The membrane material is a composite, and it is possible that the total degree of swelling could have been influenced by interactive forces between the PDMS layer and the PAN support layer. This is unlikely, however, as the effect of the support layer was considered in their work.

5. The difference between the swelling degree and the swelling ratio. The swelling degree is calculated on a mass basis whereas the swelling ratio is derived from a volumetric basis. In a different study by Vankelecom *et al.* [77], who used a mechanical press to pressurize a swollen slab of PDMS to 10 bar, it was reported that 44% of the swollen volume of PDMS was reduced due to the pressure. This value gives an indication of the degree of membrane compaction with a particular solvent, however it does not provide any information about mixtures of solvents nor how the compaction can affect the likely degree of separation.

8.3 Effect of pressure on PDMS swelling in alcohols

The degree of total polymer swelling in ethanol and isopropanol was measured at different applied pressures as shown in Figure 8-2.

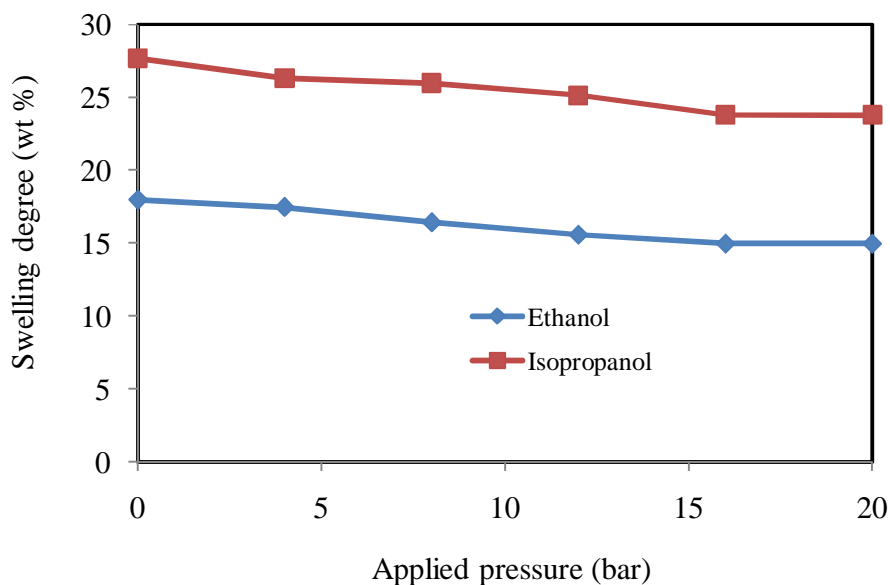


Figure 8-2 Effect of applied pressure on swelling degree of PDMS in ethanol and isopropanol

The results indicate that as applied pressure increases the swelling degree in both alcohols decreases. For ethanol the highest swelling degree was 18% at 0 bar, and the lowest swelling degree was 15% at 20 bar. For isopropanol the highest swelling degree was 28% at 0 bar and the lowest was 23.7% at 20 bar. The swelling degree in isopropanol was higher than that of ethanol at different applied pressures, which was expected due to the difference in solubility parameter between PDMS and each of the alcohols.

The reduction in swelling degree with applied pressure is likely due to polymer compaction as the polymer chains moving closer together at higher pressure, reducing the free volume available for liquid sorption. These observations agree with Koltuniewicz *et al.* [250], who suggested that membrane compaction occur during pressure-driven filtration processes, leading to a reduction in the permeability.

8.3.1 Effect of pressure on PDMS swelling in alcohol/water mixtures

Swelling in alcohol/water mixture quantifies the polymer sorption capacity; hence, its ability to selectively absorb either alcohol or water from a mixture. The experiments were designed to allow both the degree of total polymer swelling, and the alcohol composition within the polymer to be measured at different applied pressures. The sorption of a set of organic/water mixtures, comprising 30% ethanol and 30% isopropanol in water were studied and results are presented in Figure 8-3.

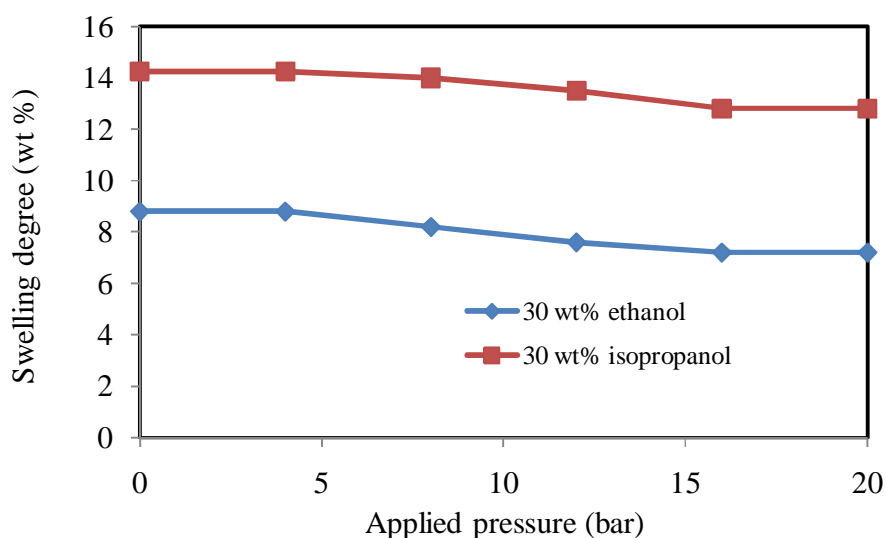


Figure 8-3 Effect of pressure on the swelling degree of PDMS in 30% alcohol/water mixtures

Figure 8-3 shows the relation between swelling degree in 30% ethanol and 30% isopropanol at different applied pressures. The results indicate that increasing the pressure leads to lower swelling degrees for both ethanol and isopropanol mixtures. In 30% ethanol the swelling degree decreases from 8.8% to 7.2%, while in 30% isopropanol it decreases from 14.2% to 12.8%.

8.3.2 Effect of applied pressure on alcohol concentration

Alcohol concentrations in the remaining liquid were determined using calibration curves, as shown in Section 3.5, and ethanol concentrations in the swollen polymers were calculated based on a mass balance as explained in Section 3.5, with the results shown in Table 8.1. Equivalent data for 30% isopropanol is shown in Table 8.2.

Table 8.1. Composition of swollen PDMS under different pressures in 30 % ethanol

Applied pressure (bar)	Ethanol concentration in swollen polymer (wt%)	Water concentration in swollen PDMS (wt%)	PDMS concentration in swollen polymer (wt%)
0	11.2	16.5	72.2
4	11.8	15.8	72.3
8	12.8	13.8	73.3
12	13.6	13.3	73.6
16	13.6	12.1	74.3
20	13.6	12.1	74.3

CHAPTER EIGHT EFFECT OF PRESSURE ON POLYMER SELECTIVITY

Table 8.2 Composition of swollen PDMS under different pressures at 30 wt% isopropanol

Applied pressure (bar)	Isopropanol concentration in swollen polymer (wt%)	Water concentration in swollen PDMS (wt%)	PDMS concentration in swollen polymer (wt%)
0	14.2	13.6	72.2
4	14.9	12.2	72.9
8	16.0	10.6	73.3
12	17.3	8.9	73.6
16	18.2	7.6	73.7
20	18.7	7.6	73.7

The results in Tables 8.1 and 8.2 show alcohol, water and PDMS concentrations in swollen PDMS at different applied pressures. These data demonstrate how the composition of the swollen polymer varies as the pressure increases from 0 to 20 bar. As expected from the data shown in Figure 8-3, the PDMS concentration increases with pressure as the amount of liquid reduces. The concentration of ethanol and isopropanol increases with increasing pressure, whereas the concentration of water decreases. The contribution of PDMS to the swollen polymer can be excluded, so that results can be interpreted in terms of alcohol/water ratio as shown in Figure 8-4.

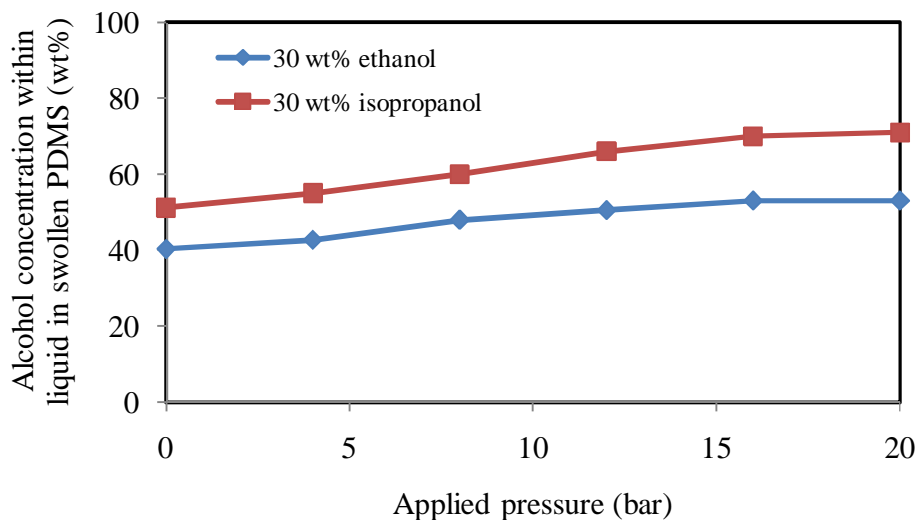


Figure 8-4 Effect of applied pressure on alcohol concentration within liquid in swollen PDMS

The alcohol concentration within liquid increases as the applied pressure increases from 0 to 20 bar. The results illustrate that the weight fraction of ethanol, and isopropanol rises from 40.3 to 52% and 62 to 72% respectively as applied pressure increases from 0 to 20 bar. In addition the concentration of isopropanol is higher than that of ethanol at different applied pressures. This is consistent with the swelling of pure component. At 0 bar alcohol concentration are 40.3% and 62% for ethanol and isopropanol respectively. This indicates that alcohol/water concentration is subjected to a fractionation at the polymer surface with preferential absorption of the alcohol. Increasing pressure cause the alcohol concentration in the liquid within swollen polymer to increase, so the ability of PDMS to selectively absorb alcohol from mixture depends on the applied pressure.

8.3.3 Effect of pressure on alcohol sorption coefficient

Sorption coefficients were calculated based on the swelling data, alcohol concentrations in aqueous solution and the corresponding concentrations in polymer. The sorption coefficients of ethanol and isopropanol are shown Figure 8-5.

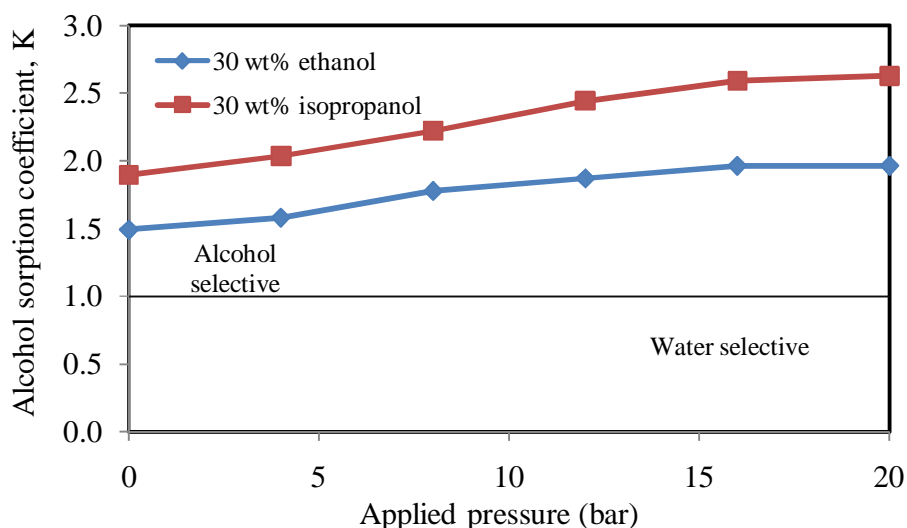


Figure 8-5 Relationship between applied pressure and alcohol sorption coefficient for 30% alcohol in aqueous mixtures

The results indicate that increasing pressure from 0 to 20 bar, leads to an increase in alcohol sorption for both ethanol and isopropanol trends. Sorption coefficients for ethanol are lower than that of isopropanol in the 30% mixtures, at all applied pressures. From 5 to 20 bar the sorption coefficient for ethanol rises from 1.49 to 1.96, and for isopropanol from 1.89 to 2.63 respectively. The results demonstrate that sorption coefficients are a function of applied pressure. At all applied pressure investigated, PDMS is selective towards alcohols in aqueous solutions and selectivity increase with the applied pressure.

8.4 Effect of pressure on PVA swelling in alcohols

The influence of applied pressure on the swelling degree of PVA in ethanol and isopropanol is presented in Figure 8-6.

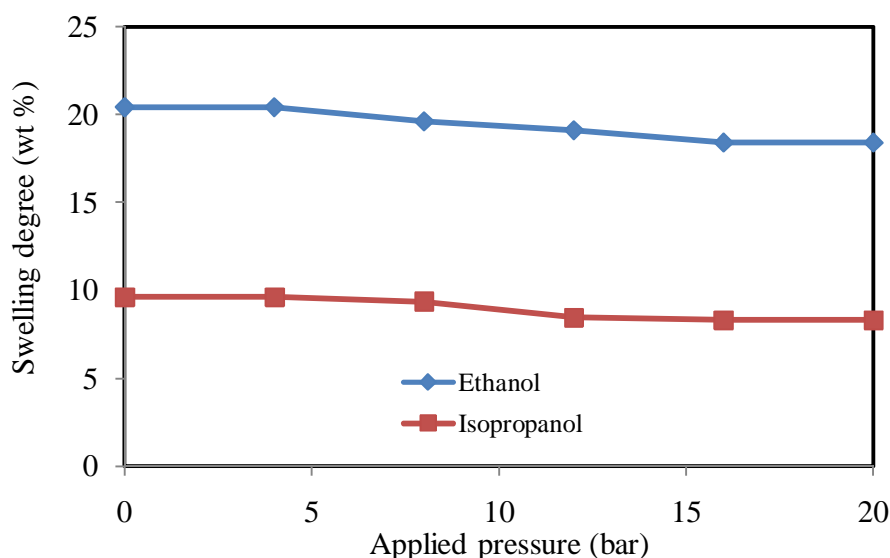


Figure 8-6 PVA swelling degree in ethanol and isopropanol at different pressure

For ethanol swelling reaches a maximum of 20% at 0 bar, and a minimum of 18.4% at 20 bar. For isopropanol the swelling is highest at 9.6% at 0 bar, and lowest at 8.3% at 20 bar. The results suggest that, as pressure is applied, PVA suffers a compression which brings polymer chains closer together, hence reducing the swelling degree. Li *et al.* [251], who observed a decrease in water flux during filtration using PVA membrane, also suggested PVA membrane compaction upon pressurisation.

8.4.1 Effect of pressure on PVA swelling in alcohol/water mixtures

The assessment of PVA/alcohol selectivity process requires the evaluation of polymer swelling in alcohol/water mixture under pressure. The influence of applied pressure on the swelling degree of PVA in 30% alcohol/water mixtures is presented in Figure 8-7.

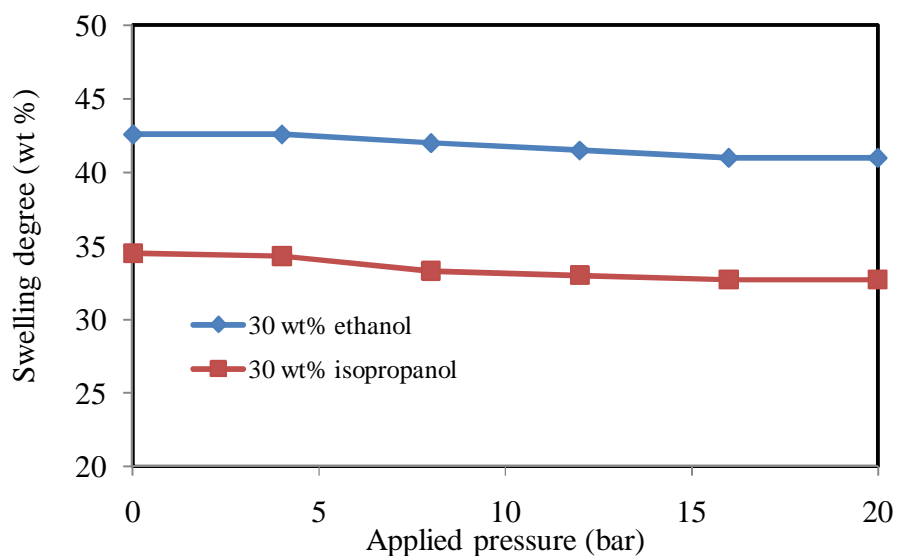


Figure 8-7 Effect of applied pressure on the swelling degree of PVA in 30% alcohol/water mixtures

The swelling degree decreases in for alcohol/water mixtures when the applied pressure increases from 0 to 20 bar. The swelling degree reaches a maximum of 42.6% and 34.5% at 0 bar, and a minimum of 41.4% and 32.7% at 20 bar for 30% ethanol and isopropanol respectively.

8.4.2 Effect of applied pressure on alcohol concentration

Equilibrium studies were extended to investigate alcohol concentration within liquid inside the swollen polymer at different applied pressures. Alcohol concentrations (%) in the remaining liquid were determined as explained in Section 3.5, the results are shown in Tables 8.3 and 8.4.

CHAPTER EIGHT EFFECT OF PRESSURE ON POLYMER SELECTIVITY

Table 8.3. Composition of swollen PVA under different pressures in equilibrium with 30% ethanol water.

Applied pressure (bar)	Ethanol concentration in swollen polymer (wt%)	Water concentration in swollen PVA (wt%)	PVA concentration in swollen polymer (wt%)
0	20.7	38.9	40.3
4	20.5	39.7	39.9
8	19.7	39.8	40.4
12	18.6	39.5	41.7
16	18.0	40.0	41.9
20	18.0	40.0	41.9

Table 8.4. Composition of swollen PVA under different pressures in equilibrium with 30% isopropanol in water mixture

Applied pressure (bar)	Isopropanol concentration in swollen polymer (wt%)	Water concentration in swollen PVA (wt%)	PVA concentration in swollen polymer (wt%)
0	12.0	46.2	41.7
4	11.4	46.7	41.8
8	10.8	46.9	42.2
12	10.0	47.2	42.8
16	9.2	48.3	42.5
20	9.2	48.3	42.5

The results in Tables 8.3 and 8.4 show alcohol, water, and PVA compositions in swollen PVA at pressures of 0 to 20 bar. The alcohol concentration in the swollen PVA decreases with increasing pressure. The contribution of PVA to the swollen polymer can be excluded, so that results can be interpreted in terms of alcohol/water ratio. Alcohol concentrations within liquid in the swollen polymer under pressure are presented in Figure 8-8.

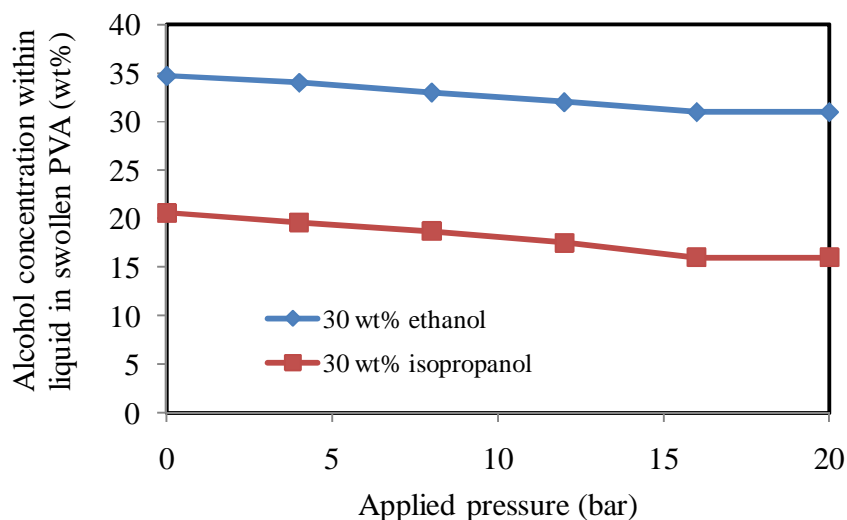


Figure 8-8 Effect of applied pressure on alcohol concentration within liquid in swollen PVA from alcohol/water mixtures.

Increasing the pressure from 0 to 20 bar cause the concentration to decreases for ethanol and isopropanol. The weight fractions of ethanol and isopropanol in the liquid absorbed in swollen polymer reduces from 34.7 to 31.5% and 20.6 to 16 % respectively. In addition, the concentration of isopropanol in liquid within the polymer is lower than that of ethanol at different applied pressures.

The results show that alcohol concentration within liquid in swollen polymer is subjected to a fractionation at the polymer surface with preferential absorption of the ethanol from ethanol/water and water from isopropanol/water mixtures.

8.4.3. Alcohol sorption coefficient (K) for PVA in alcohol/water mixture

The sorption coefficients of ethanol and isopropanol in 30% mixtures with water are shown in Figure 8-9.

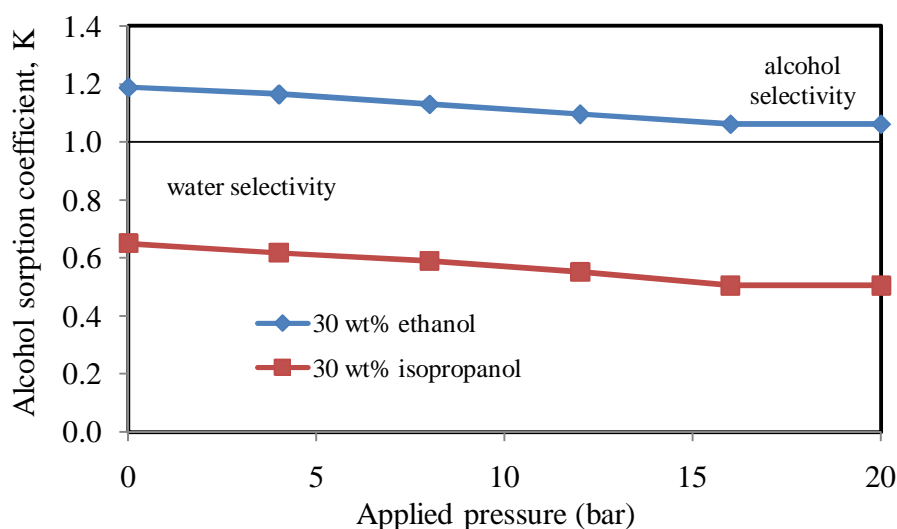


Figure 8-9 Relationship between applied pressure and the alcohol sorption coefficient from aqueous alcohol mixture

Figure 8-9 shows the effect of pressure on sorption coefficient and indicates that increasing pressure leads to a decrease in sorption coefficient for both ethanol and isopropanol. The highest sorption coefficient was 0.70 for ethanol at pressure 0 bar, and corresponding highest sorption coefficient was 0.37 for isopropanol at the same pressure. As the pressure is increased from 0 to 20 bar, the sorption coefficient decreases from 1.18 to 1.06 for ethanol, and from 0.64 to 0.50 for isopropanol.

The results demonstrate that sorption coefficients are a function of applied pressure. At all pressures investigated, the sorption coefficients are higher than 1 for ethanol, and lower than 1 for isopropanol. Therefore PVA is selective towards ethanol from ethanol/water, and water from isopropanol/water and selectivity decrease with the applied pressure.

8.5. Sorption coefficients in PDMS and PVA

The selectivity of polymers in aqueous solution has been shown to depend on the applied pressure. In order to assess polymer selectivity in a separation process, a comparison between PDMS and PVA is presented in Figure 8-10.

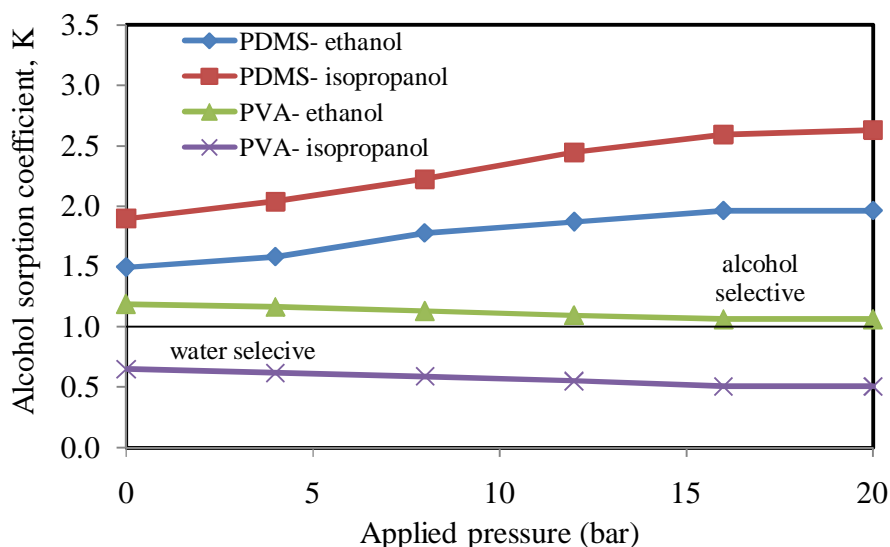


Figure 8-10 Comparison between PDMS and PVA polymers in aqueous alcohol mixture under different pressures

The results indicate that the sorption coefficient increase for PDMS and decrease for PVA as pressure increases from 0 to 20 bar. The sorption coefficient are higher than 1 for PDMS /ethanol/water, PDMS/isopropanol/water and PVA / ethanol/water and lower than 1 for PVA/isopropanol/water. PDMS and PVA are ethanol selective from water and PDMS is selective towards isopropanol from isopropanol/water mixture and PVA is water selective from isopropanol/water.

The % changes in sorption coefficient due to the increase in pressure are shown in Table 8.5, which indicates that pressure has only a small effect of the sorption coefficient

compared to change in sorption coefficient due change in the alcohol concentration from 10 to 90%. The results indicate that alcohol sorption behaviour differs based on the polymer material, as the % changes in sorption coefficient is the highest for PDMS/ethanol/water and the lowest for PVA / ethanol/water.

Table 8.5 Change in sorption coefficient due to increasing pressure

Polymer/alcohols/water systems	% change in sorption coefficient from 0- 20 bar	% change in sorption coefficient from 10- 90 wt%
PDMS /ethanol/water	27	275
PDMS /isopropanol/water	23	363
PVA / ethanol/water	11	132
PVA / isopropanol/water	26	59

8.6 Explaining the effect of pressure on alcohol sorption coefficient

The effect of pressure on the thermodynamics of the swollen polymer can be illustrated by considering the mixing and elastic deformation components of the chemical potential. The total change in chemical potential within a swollen polymer can be defined as:

$$\Delta\mu = \Delta\mu_{mix} + \Delta\mu_{el} \quad (8.2)$$

Where $\Delta\mu_{mix}$ is the change in chemical potential due to mixing and $\Delta\mu_{el}$ is the change in chemical potential due to elastic deformation. $\Delta\mu_{el}$ changes when pressure is applied, and at equilibrium $\Delta\mu = 0$. For a pressurised system $\Delta\mu_{mix}$ must therefore change in order to balance Equation 8.1, which implies that the composition of the swollen polymer must change in order to compensate for the elastic deformation.

This could provide an additional explanation as to why the sorption coefficient varies with pressure in Figure 8-10.

8.6.1. Numerical analysis to identify the effect of fugacity

When a polymer mixed with a liquid, the chemical potential of any species in the liquid equals the chemical potential of that species within the polymer at equilibrium and it is expressed as:

$$\mu_{is}^{\wedge} = \mu_{ip}^{\wedge} \quad (8.3)$$

Where μ_{is}^{\wedge} is the chemical potential of component i in the solvent mixture, and μ_{ip}^{\wedge} is the chemical potential of component i in the polymer side. The chemical potential of a substance can be further defined as [210]:

$$\mu_i^{\wedge} = \mu_i^0 + RT \ln \left(f_i^{\wedge} / f_i^0 \right) \quad (8.4)$$

where μ_i^0 is the chemical potential of pure i at temperature T and its saturation pressure, f_i^{\wedge} is the fugacity of i in a mixture, and f_i^0 is the fugacity of pure i at saturation.

By definition, the fugacity of i in a mixture can be expressed as the product of the mole fraction (C_i), the activity coefficient (γ_i) and the fugacity of pure i at the temperature and pressure of the mixture (f_i).

$$f_i^{\wedge} = C_i \gamma_i f_i \quad (8.5)$$

The fugacity of a liquid at any pressure and temperature can be expressed relative to the fugacity at saturation, as shown in Equation 8.6 [211].

$$f_i = f_i^0 \exp \left[\frac{V_l}{RT} (P - P^0) \right] \quad (8.6)$$

where V_l is liquid molar volume, P is applied pressure, and P^0 is the saturation pressure.

Based on the Antoine equation, the saturation pressure is calculated from equation [252].

$$\log P^0 = A - \frac{B}{C+T} \quad (8.7)$$

Where P^0 is the saturation pressure, A , B , and C are Antoine equation constants. Alcohol saturation pressure is equal to the alcohol fugacity ($f_i^0 = P^0$) at low pressure where ideal gas behaviour applies. Using the Antoine equation at 25 °C, the fugacity at saturation of ethanol is 79.6 mbar, and 59.1 mbar for isopropanol. The molar volume of ethanol and isopropanol are 0.058 and 0.076 m³/kmol respectively. The effect of pressure on alcohol fugacity was calculated using Equation 8.6, and the results are presented in Figure 8-11.

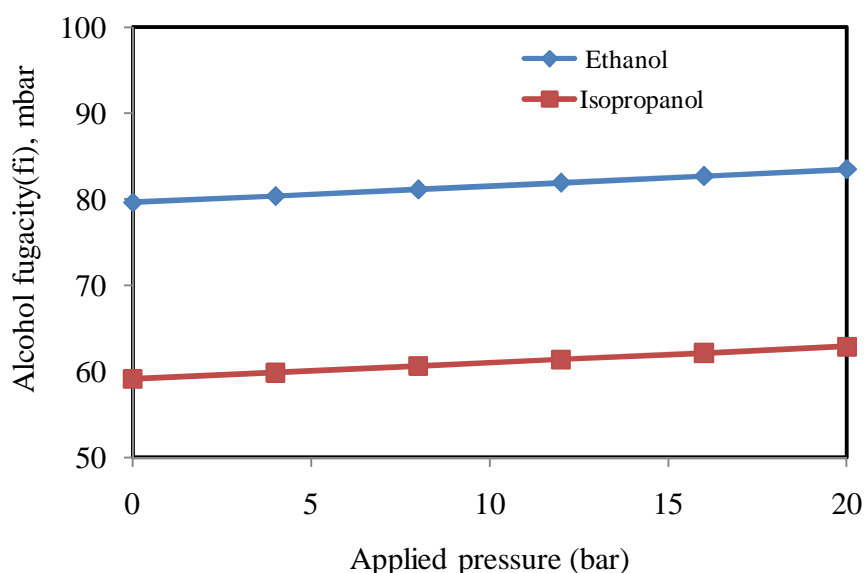


Figure 8-11 Relationship between applied pressure and alcohol fugacity for ethanol and isopropanol

The results show that as the pressure increases from 0 to 20 bar, ethanol fugacity increases from 79.6 to 83.4 mbar, and fugacity for isopropanol increases from 59.1 to 62.9 mbar. The change in fugacity is therefore relatively small across the pressure range studied; 6.5 mbar for ethanol and 4.8 mbar for isopropanol. However, the increase in sorption coefficient is 35% and 31% for ethanol and isopropanol. It is therefore unlikely that the

observed change in sorption coefficient is solely due to the effect of pressure on fugacity alone. The activity of the solvent within the swollen polymer could also be influenced by the applied pressure, and this is explored in more detail in Section 8.7.2.

8.6.2 The activity coefficient

For polymer/liquid system used in this study there are two phases; a liquid phase and a swollen polymer phase. For liquids, pressure does not affect the activity coefficient because liquids are largely incompressible. It is therefore assumed that the activity coefficient for liquid systems (γ_{il}) is independent of pressure over the range studied in this work.

Swollen polymers however are compressible, as shown in this work and by Tarleton *et al.* [253]. The assumption of incompressibility is no longer valid, and pressure could therefore affect the activity coefficient (γ_{ip}) for swollen polymer systems. The results have proven that polymers are compressed, with a corresponding change in the alcohol concentration within the polymer and also a change in sorption coefficient. The results indicate that as pressure increases from 0 to 20 bar the sorption coefficient increase in PDMS and decrease in PVA. This could lead to assume that the activity coefficient (γ_{ip}) increase in PDMS and decrease in PVA based on change the pressure. The activity coefficient profile in the swollen polymer can be represented by Figure 8.12.

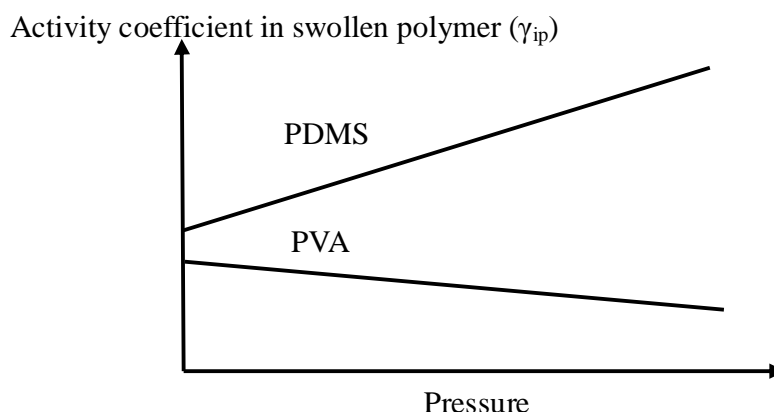


Figure 8-12 Activity coefficient profile through the swollen polymer due to increasing pressure

The schematic drawings represented by Figure 8-12 indicate that the activity coefficient (γ_{ip}) increase in PDMS and decrease in PVA based on change the pressure which in agreement with the results in Figure 8-10.

The results in Figure 8-10 indicate that alcohol sorption behaviour differs based on the polymer material, and alcohol sorption coefficient increases for PDMS, and decreases for PVA. This could be explained as the compression force moves polymer chains closer together affected the intermolecular forces between them. Hence, the activity coefficient in the polymer (γ_{ip}) changes leading to a corresponding change in sorption coefficient. The hypothesis proposed is that the sorption under pressure could be linked with the activity coefficient in the swollen polymer. As liquid activity coefficient is a constant, the change in sorption coefficient could be related to the activity coefficient in the swollen polymer only. The hypothesis in Figure 8-12 indicate that increasing pressure could lead to an increase in the activity coefficient in PDMS and decrease in the activity coefficient in the PVA.

This study suggests that pressure predominantly affects the activity coefficient in the polymer (γ_{ip}). The implications of this finding can be applied to membrane separation processes using dense membranes such as PDMS and PVA, and this is illustrated in Figure 8-13 and 8-14 for solution-diffusion and pore-flow models.

The solution diffusion model assumes a constant pressure across the membrane, therefore the activity coefficient of the swollen polymer (γ_{ip}) will remain constant. However the pore flow model assumes a smooth pressure gradient through the membrane, hence γ_{ip} will also vary across the membrane. It would be expected that the concentration in the liquid has changed on the low pressure side due to difference in activity coefficient between polymer and liquid.

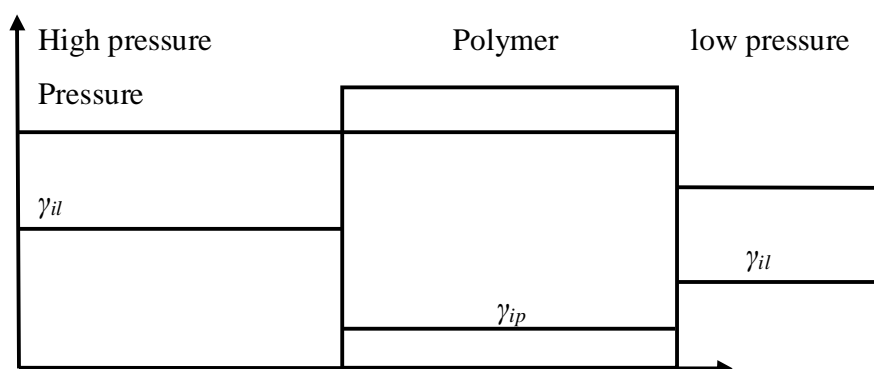


Figure 8-13 Simulation of pressure driven permeation of one component through a membrane based on solution diffusion model

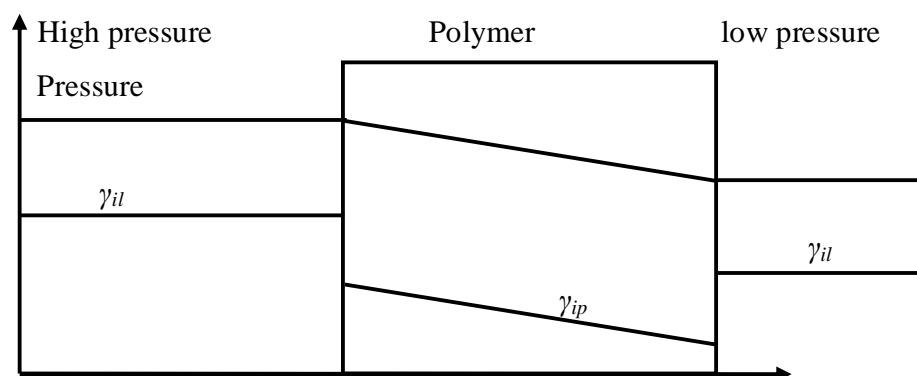


Figure 8-14 Simulation of pressure driven permeation of a one-component through a membrane based on pore flow model

The change in activity coefficient at the surface occurs because of the different sorption coefficient at both sides, which creates the separation-ability of such a membrane. For the pore flow model, the separation will be due to the activity coefficient of the polymer (γ_{ip}) and the change in activity coefficient at both sides of the polymer surface. Whether considering pore flow or solution diffusion it is the change in activity coefficient at the surface that provides the different sorption coefficient at both sides, which in turn creates the separation ability of the membrane. No separation will occur if there is no difference in the sorption coefficient at both sides of a membrane. In PDMS/alcohol/water or PVA/alcohol/water systems, due to small differences between sorption coefficients at both sides the separation would not be expected to dramatically change due to a change in pressure.

8.7 Conclusions

Increasing pressure decreases the degree of polymer swelling for PDMS and PVA in pure alcohol and aqueous alcohol solutions due to membrane compaction. Both polymers showed that selectivity is influenced by the applied pressure, as quantified by alcohol sorption coefficient, which differs based on the polymer material. Alcohol sorption coefficients increase for PDMS and decrease for PVA. The applied pressure has only a small effect on the sorption coefficient, with increasing pressure from 0 to 20 bar, the corresponding change in sorption coefficient ranges only from 10 to 27%, which indicates that pressure has only a small effect of the sorption coefficient compared to change in sorption coefficient due change in alcohol concentration.

The activity coefficient in the swollen polymer depends on the polymer type and solvent composition. The results show that the alcohol activity coefficient between polymer and liquid at high and atmospheric pressure affects the polymer selectivity, rather than a change in fugacity. The separation-ability of the polymer is due to the change in activity coefficient from the high pressure side to the atmospheric pressure side of the polymer.

This work suggests that the effect of applied pressure on selectivity could be used to enhance the predictive capability of current transport models, since the membrane thickness and sorption coefficients can be treated as variables rather than constants.

Chapter 9 CONCLUSIONS AND FUTURE WORK

9.1 Conclusions

Membrane materials for organic separation are selected empirically. This thesis presents a new idea to quantify the inherent polymer selectivity based on polymer swelling. It is generally accepted that polymer swelling plays a significant role in determining levels of polymer selectivity; therefore the degree of polymer swelling was used to quantify the selectivity of a polymer in a binary mixture. This thesis presents a systematic study to identify the key parameters affecting the poly (dimethyl siloxane) (PDMS) and poly (vinyl alcohol) (PVA) swelling process.

This work concludes that polymer materials (PDMS/PVA) and alcohol concentration have a major effect on polymer selectivity while the polymer crosslinking content and applied pressure have less significant effect on selectivity. The selectivity was evaluated for model examples such as ethanol/hexane and ethanol/heptane, these mixtures have a wide span of polarity which ranges from non polar n-heptane/n-hexane to polar ethanol. The results showed that PDMS selectivity decreased with increasing ethanol concentration in the mixture.

The swelling behaviour can be predicted by using solubility parameters. It was found that the deviation between polymer and solvent solubility parameters has a key role in predicting the degree of swelling in pure solvents. Swelling is maximal when $(\delta_p - \delta_s)$ is 0. The relationship between solubility parameter and swelling is not linear and differs for each polymer-solvent system. This was shown from the swelling results obtained from polymer swelling in n-butanol and tert-butanol. PDMS swelling degree increases with decreasing δ_h and δ_r , while PVA swelling degree increases with increasing δ_h and δ_r .

However the influence of dispersions parameter (δ_d) has a negligible influence in determining the polymer swelling degree for all solvents studied.

The molecular size of solvent plays an important role in the swelling degree, and this factor must also be considered in conjunction with the solubility parameter. In the case of alcohols, the results indicated that swelling degree in PVA decreases with an increase in carbon number, which indicates that swelling degree is also influenced by molecular size and shape.

The swelling degree in solvent mixtures depends on the mixture composition and the polymer type. Polymer selectivity changes based on the mixture type and composition. This was observed with PDMS in ethanol/n-hexane, ethanol/n-heptane, ethanol/water, and isopropanol/water. It was also observed with PVA in ethanol/water. However, PVA does not show any selectivity change and indicates that a water selective region exists for the full isopropanol concentration range.

Polymer selectivity is highly dependent on the alcohol type and the mixture composition, and the polarity and molecular size of each component are important factors which affect the polymer selectivity. The sorption behaviour arises due to molecular size and polarity, however from the presented data; it is possible to infer which is more dominant.

Further investigations of the component sorption from liquid mixture were performed by evaluating the ternary mixture system using the Flory-Huggins model. There is poor agreement between actual and predicted activities of all the studied ternary systems: PDMS/ethanol/hexane, PDMS/ethanol/heptane, PDMS/ethanol/water, PDMS/isopropanol/water, and PVA/isopropanol/water except for PVA/ethanol/water system there is agreement between actual and predicted activity in the range of 0-40 wt%.

This work confirms that the Flory-Huggins model is limited to predicting the sorption behaviour, and this limitation could be due to the assumption of constant interaction parameters.

This work demonstrated that crosslinking content influences the total swelling degree and alcohol concentration within the swollen polymer. The higher the degree of crosslinking between the polymer chains, the more alcohol-selective PDMS polymers become, and the less alcohol-selective PVA polymers become. The results indicate that polymer selectivity depends on crosslinking content and demonstrate that the selectivity of alcohol in polymers PDMS/PVA can be regulated based on the amount of the crosslinking.

The total degree of swelling is influenced by the applied pressure, mixture type and compositions. The applied pressure affects the sorption coefficient, which is thought to be due to a change in activity coefficient between polymer and liquid at high pressure. This work suggests that change in activity coefficient between high and atmospheric pressure across the polymer creates the separation-ability of such a membrane because of the different sorption coefficient at both sides. This could lead to suggested that no separation will occur if there is no difference in the sorption coefficient at both sides of a membrane. In PDMS/alcohol/water or PVA/alcohol/water systems, due to small differences between sorption coefficients at both sides the separation would not be expected to dramatically change due to a change in pressure.

9.2 Future work

It was not possible to examine all advances during the limited PhD time and some questions will remain unresolved. A brief number of ideas for possible future work are described below.

This project aimed to explore membranes that extract organics from water. Two different polymers were identified as candidate membrane materials, and the selectivity was quantified. The next step would be to fabricate a membrane and perform filtration tests.

This work has quantified that selectivity due to sorption; therefore a rigorous comparison between polymer selectivity and actual selectivity obtained from filtration data using the same membrane materials is ideally suited to assess the inherent polymer selectivity.

This work has identified the separation that occurs due to sorption; therefore, future work is required to quantify separation due to diffusion, in order to achieve overall membrane selectivity determination. Future work could identify the diffusion coefficient using the gravimetric method. The diffusion coefficient could be calculated for a block polymer as a function of the concentration based on the solvent uptake at time (t) and at equilibrium by Long's model.

$$\left(\frac{w_t}{w_\infty}\right) = \frac{16D_i t}{\pi l^2} \quad (9.1)$$

$$D_i = D_i^0 \exp(\gamma_i C_i) \quad (9.2)$$

where w_t and w_∞ are the solvent uptake at time t and at equilibrium, l is the membrane thickness, C_i is the solvent uptake (mol/m^3), D_i is the diffusion coefficient, D^0 is diffusion coefficient at zero penetrant concentration, γ_i is activity coefficient respectively.

Many questions are still open regarding the underlying mechanism affecting the sorption of solvent in polymers based on molecular size or polarity. The data obtained from this work indicate that size and polarity have a competing effect on alcohol sorption; however these data are not sufficient to identify which one is more dominant in the separation mechanism. Future work could establish the competing effect by investigating sorption of different molecular size solvents but with the same polarity, and investigating different solvents polarity but with the same size.

This work has quantified the polymer sorption characteristics, the next step is to characterize the polymer surface and find the ideal combination between polymer hydrophobicity/hydrophilicity and the sorption properties.

Swelling effect on polymer structure is studied using different crosslinking content in this thesis. Next step will be quantifying these effects using AFM which will provide more understanding of the effects of these variables on polymer selectivity.

This work has identified that a change in sorption coefficient occurs due to the activity coefficient, and confirmed the unpredicted behaviour of the activity coefficient. Further work is required to understand the fundamental mechanisms of the activity coefficient in swollen polymers and its role in polymer selectivity.

The work has proven that the Flory-Huggins theory could not be used mathematically to describe the ternary system of polymer/alcohol/water, so the development of a mathematical model capable of describing the ternary system will be a challenge. This model should consider the change in χ_{s1s2} of alcohol/water, and so future work should attempt to develop a model with variable interaction parameters rather than constant ones.

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APPENDIX 1

Appendix 1

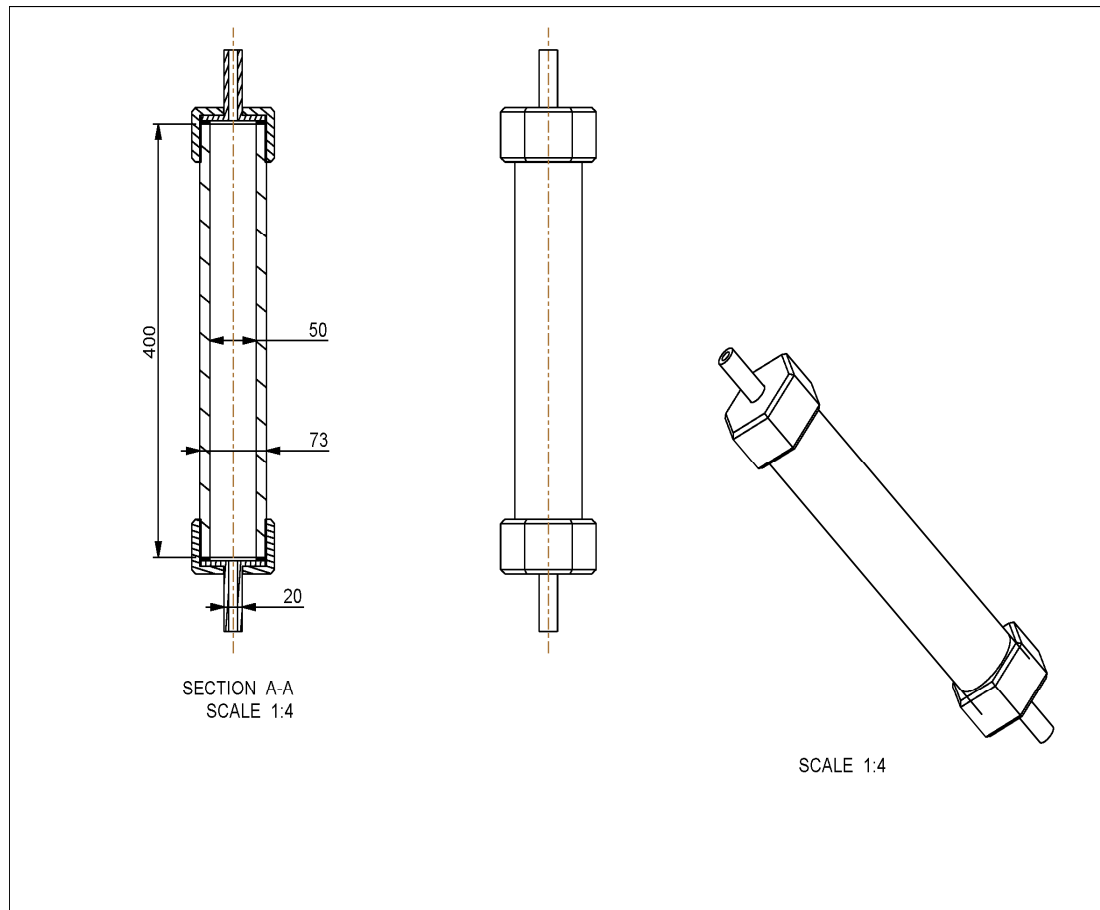


Figure 15 Pressure cell mechanical designs

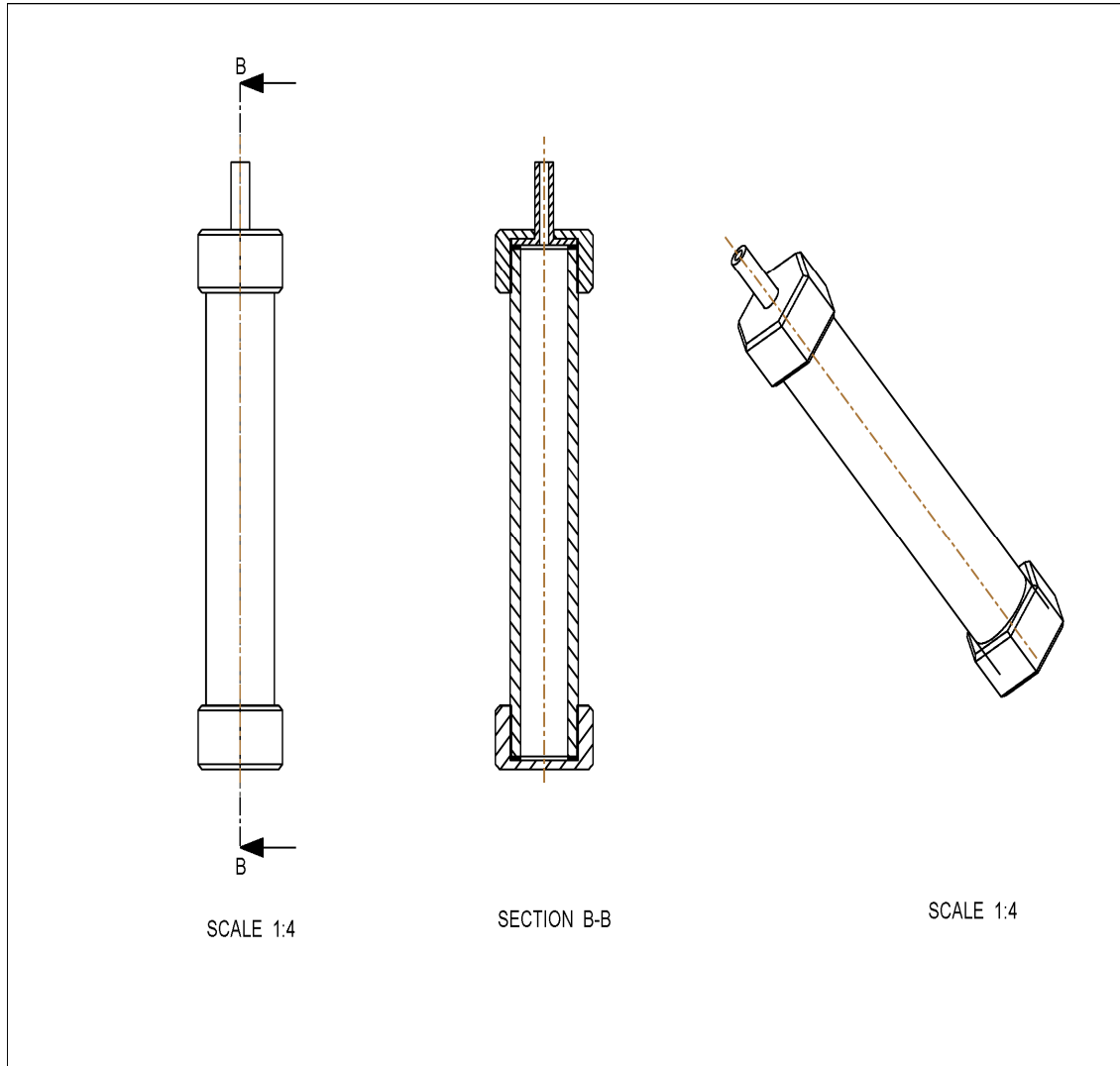


Figure 16. Reservoir cell mechanical design

Publications from this thesis

Peer review publication

- 1- Farid, O. M., Robinson, J. (2009) Removal of organics from wastewater using nanofiltration, Journal of Filtration Society. 9(4): pp. 295-300.

Conferences papers

- 2- Farid, O. M., Robinson, J. (2009) Effect of polymer swelling on the nanofiltration performance of poly(dimethyl siloxane), presented in EUROMEMBRANE 2009, France.
- 3- Farid, O. M., Robinson, J. (2009) Effect of polymer swelling on the nanofiltration performance of poly(vinyl alcohol), presented in FILTECH Europe 2009, Germany.